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# THIN FILM CONDUCTIVE COATINGS FOR SURFACE HEATING AND DECONTAMINATION

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This set of equations are then made nondimensional by suitably chosen dimensionless groups and programmed for solution by finite-difference methods. A listing of the program together with the required input parameters is given.

The program is capable of predicting the temperature and the contaminant concentration of a solid undergoing heating. Some special cases have been run to exhibit the typical behavior of such systems. For most cases the heating decontaminates the solid. However, for some cases the heating increases the solubility of the contaminant and may increase its concentration after long periods. Further work to analyze and overcome this problem is recommended. The generalization of the present code to allow for chemisorption, variable physical properties, multicomponent adsorption and optimal heating is also recommended. In addition, experimental data required for using the code are stated and some experiments are suggested.

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## PREFACE

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## THIN FILM CONDUCTIVE COATINGS FOR SURFACE HEATING AND DECONTAMINATION

### 1. INTRODUCTION

The problem of contamination of solids by chemical vapors is one of important consideration for the design of military vehicle components. Typically, a vehicle exposed to undesirable vapors will undergo contamination by the vapors being adsorbed on solid surfaces. After long periods of exposure, absorption of the vapor into the solid will take place. This can cause deterioration of materials such as plexiglass windows and may result in the entire unit being temporarily nonfunctional.

In the present analysis we examine the process of decontamination by heating the plexiglass substrates with imbedded electrically conducting layers. The application of such heating elements for the purpose of deicing is well known. However, little is known about its overall effectiveness for the removal of adsorbed and absorbed contaminants. While the heat input supplies energy to the contaminant molecules and sets them into a free state (gaseous state), it also increases the solubility of the contaminant in the solid substrate. It is therefore necessary to carry out a detailed mathematical analysis to determine the effect of heating on adsorbed and absorbed contaminants.

In the current development we first present an overview of adsorption/desorption kinetics and then develop a one-dimensional model for the removal of physically adsorbed contaminants. The mathematical analysis provides information as to what data are needed to predict the performance of such a decontamination system. At the same time some typical cases have been run to simulate such prediction. Also included are cases for which the increased solubility due to heating may cause the contaminant level to increase.

Further to the conclusion drawn from this analysis, recommendations are made for future studies. In particular, calculations for optimal heating levels to minimize material

damage by heat are needed. In addition, the analysis of multiple-element decontamination systems and further development to handle chemisorption and multi-component contaminants are very much needed in order to establish design guidelines.

## 2. KINETIC THEORY OF ADSORPTION AND DESORPTION

### 2.1 Fundamentals

When the molecules of a gas strike another solid or liquid surface, they tend to cling to the surface for a certain length of time before going back to the gas phase. Such behavior can lead to a high concentration of these molecules on the surface. This phenomenon is known as adsorption. Molecules may be adsorbed either physically or chemically. Physical adsorption takes place due to the Van der Waals forces. Chemical adsorption (or chemisorption) occurs due to an exchange or sharing of electrons or ions between the striking molecules and the molecules of the surface.

The striking molecules when adsorbed enter a bound state thereby releasing some energy. This release of energy is known as the heat of adsorption. If an adsorbed molecule is supplied with this energy, it will desorb from the surface and go into the gaseous state. In the case of physical adsorption, the heat of adsorption is about 10 kilocalories per mole. For chemisorption it may be as high as 100 kilocalories per mole. The adsorption time may be of the order of microseconds for physical adsorption. In the case of chemisorption, it is usually several seconds but may, in some instances, be as high as several years. For both regimes of adsorption these times are usually several orders of magnitude larger than the thermal vibration time of the molecules of the adsorbent. Therefore, the number of molecules,  $\sigma$ , adsorbed at any given instant is given by

$$\sigma = nt \quad (2.1)$$

where  $n$  is the number of molecules striking a unit area per unit time and  $t$  is the adsorption time.

The number flux at the surface, for an ideal gas, is given by the following well-known relationship from kinetic theory:

$$n = \frac{Np}{(2\pi MRT)^{1/2}} \quad (2.2)$$

where  $N$  is the Avogadro number,  $p$  is the gas pressure,  $M$  is the molecular weight of the gas,  $R$  is the universal gas constant and  $T$  is the temperature.

The adsorption time  $\tau$  is related to the gas temperature and the heat of adsorption by

$$\tau = \bar{\tau} e^{Q/RT} \quad (2.3)$$

where  $\bar{\tau}$  is the oscillation period of the molecules and  $Q$  is the molar heat of adsorption/desorption. If we assume that all the molecules striking the surface are adsorbed, then by combining (2.1-2.3) we see that

$$\sigma = \frac{Np}{(2\pi MRT)^{1/2}} \bar{\tau} e^{Q/RT} \quad (2.4)$$

Therefore, for given vapor adsorbate and adsorbent surface, at constant temperature, we have the following isotherm:

$$\sigma = k_o p \quad (2.5)$$

where  $k_o$  is a constant.

The number of molecules per unit area undergoing desorption by thermal excitation is given by

$$n_v = v \sigma e^{-Q/RT} \quad (2.6)$$

where  $v$  is a factor of proportionality with units of  $\text{sec}^{-1}$ . At equilibrium, therefore,  $n = n_v$  and  $v = 1/\bar{\tau}$ , so that  $\sigma = n \bar{\tau} e^{Q/RT}$  as stated earlier.

If all the molecules striking a surface are not adsorbed and a fraction  $\alpha$  is reflected, then  $n$  is reduced by a factor  $(1-\alpha)$ . To accommodate for this we define an apparent time constant  $\tau' = (1-\alpha)\bar{\tau}$  and use it instead of  $\bar{\tau}$ .

The adsorption isobar may be identified from (2.4) by holding  $p$  constant. This gives

$$\sigma = \frac{k_1 e^{Q/RT}}{T^{1/2}} \quad (2.7)$$

Since the  $T^{1/2}$  dependence is rather weak, we may write

$$\sigma \approx k_1 e^{Q/RT} \quad (2.8)$$

Similarly at constant  $\sigma$  we may identify the isostere as

$$p \approx k_2 e^{-Q/RT} \quad (2.9)$$

By taking the logarithm of each side of equation (2.9) we may write

$$\ln p = -\frac{Q}{RT} + B_a \quad (2.10)$$

where  $B_a = \ln k_2$  is a constant. This equation is similar to the expression for the vapor pressure as a function of temperature,

$$\ln(p_o(T)) = -\frac{Q}{RT} + B_o \quad (2.11)$$

By defining  $x = p/p_o$  and combining (2.10) and (2.11) we have

$$\ln x = \ln(p/p_o) = -\frac{Q-Q_o}{RT} \quad (2.12)$$

Differentiation with respect to  $T$  leads to

$$\frac{\partial \ln x}{\partial T} = \frac{Q-Q_o}{RT^2} \quad (2.13)$$

where we have the dependence of  $Q$  and  $Q_o$  on  $T$  is taken to be negligible.

## 2.2 Langmuir's Adsorption Isotherm

It was assumed by Langmuir<sup>1</sup> that adsorption in the form of a monomolecular layer takes place at a constant heat of adsorption  $Q$ . It was further assumed that the molecules that strike the covered portion of the interface would be reflected instantaneously. In other words, the residence time for these molecules is zero. The

number of adsorbed molecules in such a case is proportional to the unused sites and is given by

$$\sigma = n' \tau = n(1 - \sigma/\sigma_0) \tau \quad (2.14)$$

where  $\sigma_0$  is the maximum number of available adsorption sites per unit area. By defining a fraction  $\theta = \sigma/\sigma_0$ , and noting that from (2.1) and (2.5) we have  $n\tau = k_0 p$ , we obtain

$$\theta = \frac{k_0 p}{1 + k_0 p} \quad (2.15)$$

where  $k_0 = k_0/\sigma_0$ .

This model for adsorption is suitable for low pressures and is particularly applicable to chemisorption for which we have a monomolecular layer.

### 2.3 Multilayer Adsorption

A model for multilayer adsorption was suggested by Brunauer, Emmett & Teller<sup>2</sup> in 1938. A schematic for this model is shown in Fig. 2.1 below. Here the regular stacking of the molecules is shown for illustrative purposes only. Actually, the molecules would be randomly distributed over the entire surface under consideration.

In the model, the fraction of the surface covered by  $i$  layers of molecules is denoted by  $\theta_i$ . It is assumed that for  $i > 1$ , the heat of adsorption  $Q_0$  is constant and is identified as the latent heat of condensation. This is due to the fact that the energy exchange takes place between like molecules as it does in the case of condensation. For  $i = 0$  the heat of adsorption while capturing a monolayer of molecules is denoted by  $Q_0$ , and taken to be a constant. Generally we have  $Q_0 > Q_0$ .

In order to maintain the fraction  $\theta_0$  as constant, the number of molecules adsorbed on the uncovered portion must be equal to the number of molecules desorbed from  $\theta_0$  per unit time per unit area. This would correspond to an equilibrium state for  $\theta_0$ . Hence we have

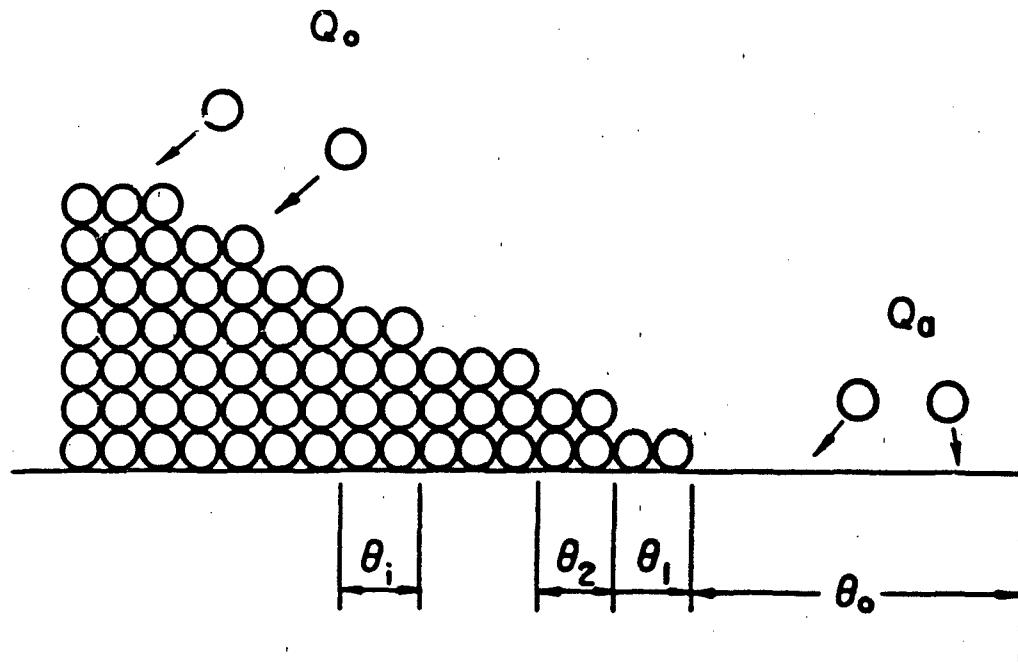


Fig. 2.1  
A schematic of multilayer adsorption kinetics

$$n\theta_o = v_o \sigma_o \theta_1 \quad (2.16)$$

where  $v_o$  is the proportionality constant similar to the one defined in (2.6). For  $i = 1$  the fraction  $\theta_1$  is maintained constant by adsorption and desorption at  $\theta_1$  to or from  $\theta_o$  and  $\theta_2$ . By simple molecular balance we have

$$n\theta_o + v_1 \sigma_o \theta_2 = v_o \sigma_o \theta_1 + n\theta_1 \quad (2.17)$$

It is clear to see that from (2.16),

$$n\theta_1 = v_1 \sigma_o \theta_2 \quad (2.18)$$

Similarly, it can be proved that

$$n\theta_{i-1} = v_{i-1} \sigma_o \theta_i \quad (2.19)$$

where

$$v_{i-1} = \frac{1}{T_{i-1}} \quad (2.20)$$

If we set  $T_1 = T_2 = T_3 = \dots$ , then

$$\theta_1 = \frac{n\tau_0\theta_0}{\sigma_0} \quad (2.21)$$

$$\theta_i = \frac{n\tau_i\theta_{i-1}}{\sigma_0}, \quad i > 2. \quad (2.22)$$

By letting  $y = n\tau_1/\sigma_0$ , (2.21-2.22) may be written as

$$\theta_1 = \frac{\tau_0}{\tau_1} y \theta_0 \quad (2.23)$$

and

$$\theta_{i+1} = y\theta_i, \quad i > 1 \quad (2.24)$$

It can now be readily shown that

$$\theta_i = \frac{\tau_0}{\tau_1} y^i \theta_0 \quad (2.25)$$

Since the layer  $\theta_i$  has a stack of  $i$  molecules (see Fig. 2.1), the total number of adsorbed molecules is proportional to

$$\begin{aligned} \theta_i &= \sum_{i=1}^{\infty} i\theta_i \\ &= \frac{\tau_0}{\tau_1} \sum_{i=1}^{\infty} iy^i \\ &= \frac{\tau_0\theta_0}{\tau_1} \frac{y}{(1-y)^2} \end{aligned} \quad (2.26)$$

Also,

$$\begin{aligned} \theta_0 &= 1 - \sum_{i=1}^{\infty} \theta_i \\ &= 1 - \frac{\tau_0}{\tau_1} \theta_0 \sum_{i=1}^{\infty} y^i \\ &= 1 - \frac{\tau_0\theta_0}{\tau_1} \frac{y}{1-y} \end{aligned}$$

which yields

$$\theta_0 = \frac{1-y}{1-y + \frac{\tau_0}{\tau_1} y} \quad (2.27)$$

We may therefore write (2.26) as

$$\theta = \frac{\frac{T_0}{T_1} y}{(1-y)(1-y + \frac{T_0}{T_1} y)} \quad (2.28)$$

Here  $\theta$  may be greater than unity for multilayer adsorption.

Noting that  $y = n\tau_1/\sigma$  and with the use of (2.2) we see that at constant temperature,

$$y = p/q \quad (2.29)$$

where  $p$  is the pressure and  $q$  is a constant. This constant can be usually identified as the saturation pressure  $p_0(T)$  (see (2.11-2.12)) and hence,

$$y = x = p/p_0 \quad (2.30)$$

As a result (2.28) can be written as

$$\theta = \frac{kx}{(1-x)(1-x + kx)} \quad (2.31)$$

where  $k = T_0/T_1$ . By using (2.3) we may express  $k$  as follows

$$k = \frac{T_0 e^{Q_0/RT}}{T_1 e^{Q_0/RT}} \quad (2.32)$$

where  $T_0$  and  $T_1$  refer to the thermal oscillation times on the adsorbent surface and a previously adsorbed layer, respectively. As a simplification, one may set  $\tau = \bar{\tau}$ , since the temperature dependence is the more significant factor. Equation (2.32) then reduces to

$$k = e^{(Q_0 - Q_0)/RT}$$

#### 2.4 The Heat of Adsorption

For the purpose of calculating the total heat of adsorption, we examine the schematic shown in Fig. 2.2.

The total consists of a contribution  $[(1-\theta_0)Q_0/N]\sigma_0$  for the first layer and  $[\theta_0 - (1-\theta_0)](Q_0/N)\sigma_0$  for the subsequent layers. Here  $N$  is the Avogadro number. Hence the total heat of adsorption is given by

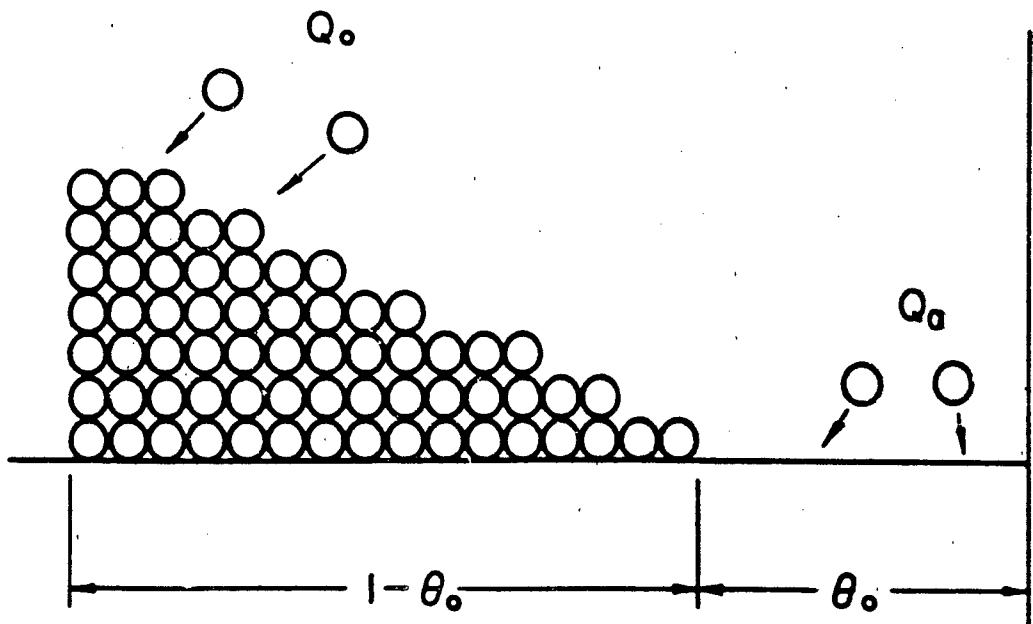


Fig. 2.2  
A schematic of total heat of adsorption calculation

$$Q_t(\theta) = [(Q_a - Q_o) + Q_o \theta] \sigma_o / N \quad (2.33)$$

At equilibrium we have

$$\theta_o = \frac{1-x}{1-x + kx} \quad (2.34)$$

and

$$1 - \theta_o = \frac{kx}{1-x + kx} = \theta(1-x) \quad (2.35)$$

With a little algebra it can be shown that

$$Q_t(\theta) = [Q_a - (Q_a - Q_o)x] \theta \sigma_o / N = Q \theta \sigma_o / N \quad (2.36)$$

where we define  $Q$  as

$$Q = Q_a - (Q_a - Q_o)x \quad (2.37)$$

## 2.5 Limits of Validity and Further Approximations

For  $x \ll 1$  we have  $Q \rightarrow Q_a$  as expected for monolayer adsorption. As  $x \rightarrow 1$ ,  $Q \rightarrow Q_o$  representing a near-saturation condition.

The adsorption isotherm of the form  $\theta \propto p$  is valid only for extremely low partial pressures. This model predicts no saturation and is not valid for  $p = p_o$ . The Langmuir isotherm of the form  $\frac{\theta}{1-\theta} \propto p$  (or  $\theta = \frac{k_3 p}{1+k_3 p}$ ) is valid only for monolayer adsorption. For  $Q_a \gg Q_o$  and  $\tau_i \ll \tau_c$  ( $i > 1$ ), the multilayer results reduce to the Langmuir model. In the case of pure chemisorption or for physical adsorption at low pressures, the behavior as predicted by the Langmuir model is observed.

The multilayer adsorption of Brunauer et al.<sup>2</sup> is based on constant adsorption times for layers corresponding to  $i > 2$  (above the monolayer). Some simplifications are also proposed by identifying the heat of adsorption (which is taken as a constant) for higher layers with the latent heat of condensation  $Q_o$ . The identification of  $q$  as  $p_o(T)$  in (2.29) is an additional simplification which seems quite attractive. However, there are situations in which this approximation is not valid. This multilayer adsorption model is applicable over a wide range of pressures.

The fundamental principle behind the decontamination lies in behavior of  $\theta$  with temperature. From (3.31) it is clear that for small  $x$ ,  $\theta$  is nearly proportional to  $x$ . However  $p_o(T)$  increases with  $T$  and hence  $x = p/p_o$  decreases with  $T$ . Therefore  $\theta$  decreases with  $T$ , indicating a reduction in the amount of contaminant adsorbed in the surface of the solid. It is clear that by raising the temperature a surface may be decontaminated.

In the next section we formulate the governing differential equations for substrates electrically heated by imbedded conductive layers.

### **3. DECONTAMINATION OF SUBSTRATES BY ELECTRICAL HEATING: FORMULATION**

#### **3.1 Description of Problem**

Since with a rise in the temperature of the substrate, decontamination of the surface takes place, the possibility of heating by imbedded elements (such as in an automobile windshield) is considered here. The application to defogging and deicing is well known.<sup>3,4,5,6</sup> We adopt here a one-dimensional model in which the heat and mass flow in the direction parallel to the plane of the substrate are considered negligible. At this point we can define a specific one-dimensional time-dependent problem.

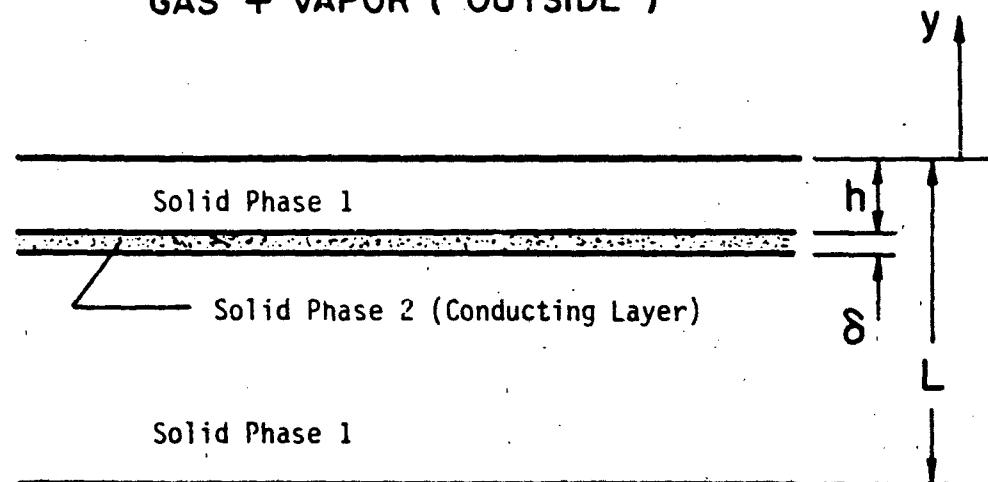
Let us consider a long slab of thickness  $L$  which is exposed to an environment containing a chemical vapor and some inert gases. An electrically heated layer of thickness  $\delta$  is imbedded in the slab to a depth  $h$  (see Fig. 3.1). The substrate is referred to as phase 1 and the heating element as phase 2. The chemical vapor deposits itself on the surface of the substrate by adsorption and then diffuses into the bulk of the substrate.

**The physico-chemical processes involved are as follows:**

#### **Mass Transfer**

1. Diffusion and convection of contaminant vapor in the environment takes place due to the wind pattern, or to the motion of the substrate. This sets up a velocity profile near the surface of the substrate. As a result, convective transport of the contaminant to or from the surface takes place.
2. Adsorption/desorption of the vapor at the solid surfaces.
3. Diffusion of vapor into the solid phases (1 and 2). Chemical reactions within the solid are not being considered.

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Fig. 3.1

One-dimensional model of substrate with imbedded heating element

### Heat Transfer

1. Heat release by electrical heating within the conductive layer.
2. Heat conduction in the solid phases 1 and 2.
3. Heat associated with adsorption/desorption at the surface.
4. Thermal diffusion and convection in the gaseous environment.

### Assumptions

1. Fluid flow processes are considered only for their effects on heat/mass transfer. Simple lumped parameter models (i.e., heat and mass transfer coefficients) are to be used for these processes.
2. The adsorbate (solid) is infinite in length. A one-dimensional formulation is used for the solid phase.
3. A uniform volumetric heat generation rate  $q'''$  is considered in the conductive layer of thickness  $\delta$ . Any chemical reactions within the solid phase and the latent heat release thereof is not considered.
4. The concentration of the sorbed species within the solid is linearly related to the surface concentration of the adsorbed layer within certain limits.

5. The solid surfaces are taken to have reached an adsorption equilibrium with the surrounding gas-vapor mixture. At this equilibrium, the "fraction" of the surface covered ( $\theta$ ) depends on the surface temperature  $T_s$  and the partial pressure  $p_{v,s}$  of the vapor adjacent to the surface. Furthermore, at equilibrium,  $p_{v,s}$  is purely a function of the surface temperature and the heat of adsorption.

If  $p_{v,s}$  is different from  $p_{s,\infty}$  (the far-field partial pressure) then vapor transport takes place in the gaseous phase as well.

6. For the present model, only physical adsorption is treated for a multi-molecular adsorbed layer. The heat of adsorption for the first layer,  $Q_a$ , taken to be different from the subsequent layers, for which it is taken to be the latent heat of condensation,  $Q_c$ . For the first layer  $Q_a$  actually varies with the fraction covered but here we take it to be the average value.

7. The dependence of the partial pressure with temperature is given by

$$p_{v,s} = x p_{o,s} = x p_{o,\infty} e^{-\frac{Q_c}{R} \left( \frac{1}{T_s} - \frac{1}{T_\infty} \right)} \quad (3.1)$$

where  $x = m_{v,s}$  is the mole fraction of the vapor in the air adjacent to the surface.

### 3.2 Governing Equations

At this point the problem may be precisely cast into a mathematical form as a closed set of partial differential equations. With the assumptions made in §3.1, the equations for heat and mass balance are as follows:

#### Gas Phase

Heat transfer between solid surface and air:

$$q_g = h_{gt} (T_s - T_\infty) \quad (3.2)$$

Vapor mass flux between solid surface and air:

$$i_{g,v} = h_{gm} \rho_g (m_{v,s} - m_{v,\infty}) \quad (3.3)$$

where

$$h_{gt} = N_u k_g / L \quad (3.4)$$

$$h_{gm} = N_u m D_{gv} / L \quad (3.5)$$

with

$\text{Nu}$  = Nusselt number  
 $k_g$  = thermal conductivity of gas  
 $m_v$  = mole fraction of the vapor  
 $D_{gv}$  = binary diffusion coefficient between vapor and air  
 $\rho$  = density.

Equations (3.2) and (3.3) are based on lumped parameter modeling of the convective transport. The Nusselt numbers,  $\text{Nu}_t$  and  $\text{Nu}_m$  depend on the external flow conditions. The general characteristics of these Nusselt numbers are available in most heat transfer textbooks (see, e.g., Burmeister<sup>7</sup>).

#### Solid-Gas Interface

##### Heat transfer at the interface:

$$q_g = q_a = q_s \quad (3.6)$$

where

$$q_s = -k \frac{\partial T_1}{\partial y} \Big|_{y=0}$$

or

$$q_s = +k \frac{\partial T_1}{\partial y} \Big|_{y=-L} \quad (3.7)$$

and  $q_s$  is the heat release by adsorption.

##### Mass transfer at the interface:

$$j_{g,v} + j_a = j_{s,v} \quad (3.8)$$

where

$j_a$  = mass rate of adsorption ( $\text{g}/\text{cm}^2\text{-sec}$ )  
 $j_{s,v}$  = mass flux from the solid

$$j_{s,v} = -D_{1v} \frac{\partial c_{1v}}{\partial y} \Big|_{y=0}$$

or

$$(3.9)$$

$$j_{s,v} = +D_{iv} \frac{\partial c_{1v}}{\partial y} \Big|_{y=-L}$$

and  $j_{g,v}$  is given by (3.3).

### Adsorption Equilibrium

From (3.31)

$$\theta = \frac{kx}{(1-x)(1-x+kx)} \quad (3.10)$$

where

$$k = e^{(Q_a - Q_o)/RT} \quad (3.11)$$

and following (2.37) it can be seen that

$$Q = Q_o = (Q_a - Q_o)(1-x) \quad (3.12)$$

By employing the quasi-equilibrium assumption we may write the adsorption heat flux as

$$q_a = \frac{\sigma_o}{N} \theta Q \quad (3.13)$$

and

$$j_a = \frac{\sigma_o}{N} \theta x M_v = m \sigma_o \theta \quad (3.14)$$

where  $N$  is the Avogadro number,  $\sigma_o$  is the maximum number of available sites per unit area,  $M_v$  is the molecular weight of vapor, and  $m$  is the mass of one molecule of the vapor.

### Solid Phase 1

#### Heat transfer:

$$\frac{1}{\alpha_1} \frac{\partial T_1}{\partial t} = \frac{\partial^2 T_1}{\partial y^2} \quad (3.15)$$

where  $\alpha_1$  is the thermal diffusivity and  $T_1$  is the temperature.

Mass transfer:

$$\frac{1}{D_{1v}} \frac{\partial c_{1v}}{\partial t} = \frac{\partial^2 c_{1v}}{\partial y^2} \quad (3.16)$$

where  $D_{1v}$  is the diffusion coefficient, and  $c_{1v}$  is the mass concentration in  $\text{g/cm}^3$ .

We assume a linear relationship between the superficial mass concentration that is adsorbed at the surface and the volumetric concentration adjacent to the surface. This is the basis of assumption 4 in § 3.1. Thus at  $y = 0$  and  $y = -L$ ,

$$m\sigma_0 \theta = \phi c_{1v} \quad (3.17)$$

where  $\phi$  is a constant with dimensions of length. This is called the penetration depth.

The relationship (3.17) is used for cases when

$$\frac{m\sigma_0}{\phi} \ll c_0 \quad (3.18)$$

where  $c_0$  is the maximum possible concentration.

Solid Phase 2

Heat transfer:

$$\frac{1}{\alpha_2} \frac{\partial T_2}{\partial t} = \frac{\partial^2 T_2}{\partial y^2} + \frac{\dot{q}''''}{k_2} \quad (3.19)$$

where  $\dot{q}'''$  represents the volumetric heat generation rate in  $\text{cals/cm}^3\text{-sec}$ .

Mass transfer:

$$\frac{1}{D_{2v}} \frac{\partial c_{2v}}{\partial t} = \frac{\partial c_{2v}}{\partial y^2} \quad (3.20)$$

The boundary condition between solid 1 and solid 2 at  $y = -h$  and  $y = -(h+\delta)$  are

$$T_1 = T_2 \quad (3.21)$$

$$k_1 \frac{\partial T_1}{\partial y} = k_2 \frac{\partial T_2}{\partial y}$$

and

$$c_{1v} = c_{2v}$$

(3.22)

$$D_{1v} \frac{\partial c_{1v}}{\partial y} = D_{2v} \frac{\partial c_{2v}}{\partial y}$$

The initial conditions are

$$T_1 = T_2 = T_\infty \quad \text{at } t = 0$$

(3.23)

$$c_{1v} = c_{2v} = 0 \quad \text{at } t = 0$$

The equations (3.1-3.23) form a closed set. At this point it is convenient to identify dimensionless groups and make these equations non-dimensional.

### 3.3 Dimensionless Grouping

The dimensionless parameters are selected as follows:

$$Nu_t = \frac{h_t L}{k_g} \quad (3.24)$$

$$Nu_m = \frac{h_m L}{D_{gv}} \quad (3.25)$$

$$\epsilon = \frac{m\sigma_o}{\phi c_o} \quad (3.26)$$

$$\Delta = \frac{m\sigma_o c_o R}{L c_o \rho_1 c_{p1}} \quad (3.27)$$

$$H = \frac{m\sigma_o}{L c_o} \quad (\text{dimensionless adsorption depth}) \quad (3.28)$$

$$Q_o = \frac{Q_o}{RT_\infty} \quad (3.29)$$

$$Q_a = \frac{Q_a}{RT_\infty} \quad (3.30)$$

$$\delta_0 = \frac{\rho_\infty}{c_0} \text{ (ratio of saturation density at infinity to maximum solubility in solid 1)} \quad (3.31)$$

$$r_\infty = \text{vapor mole fraction at infinity} \quad (3.32)$$

$$\dot{q}^* = \frac{\dot{q} \rho_\infty L^2}{k T_\infty} \text{ (dimensionless volumetric heating rate)} \quad (3.33)$$

$$\epsilon = \frac{m \sigma_0}{\phi c_0} \text{ (dimensionless penetration depth)} \quad (3.34)$$

$$\phi_{kg} = k_g/k_1 \quad (3.35)$$

$$\phi_{Dg} = D_{gv}/D_{1v} \quad (3.36)$$

$$Le_1 = \alpha_1/D_{1v} \quad (3.37)$$

$$\phi_{as} = \alpha_2/\alpha_1 \quad (3.38)$$

$$\phi_{Ds} = D_{2v}/D_{1v} \quad (3.39)$$

$$\phi_{ks} = k_2/k_1 \quad (3.40)$$

$$T^* = T/T_\infty \quad (3.41)$$

$$c_{1v} = c_{1v}/c_0 \quad (3.42)$$

$$y^* = y/L; h^* = h/L; \delta^* = \delta/L; t^* = \alpha_1 t/L^2 \quad (3.43)$$

By combining (3.2), (3.6), (3.7) and (3.13) we obtain

$$Nu_t \phi_g (T_s - 1) - \Delta \frac{d\theta}{dt} [Q_0 + (Q_s - Q_0)(1-x)] = \pm \frac{\partial T_1}{\partial y} \text{ at } y = 0 \text{ or } y = -L \quad (3.44)$$

Similarly, by combining (3.1), (3.3), (3.8), (3.9) and (3.14) we find

$$Nu_m \phi_{Dg} \delta_0 r_\infty - \frac{x}{T_s} \frac{Q_0 (1 - 1/T_s)}{c_{1v}} - Le_1 H \theta = \pm \frac{\partial c_{1v}}{\partial y} \text{ at } y = 0 \text{ or } y = -L \quad (3.45)$$

The adsorption equilibrium given by (3.10) and (3.12), when non-dimensionalized,

gives

$$\theta = \frac{kx}{(1-x)(1-x+kx)} \quad (3.46)$$

with

$$k = \theta \frac{(Q_a^* - Q_0^*)/T_s}{(1-\theta)} \quad (3.47)$$

The remaining equations may be written as

$$\frac{\partial T_1^*}{\partial t^*} = \frac{\partial T_1^*}{\partial y'^2} \quad (3.48)$$

$$\frac{\partial c_{1v}^*}{\partial t^*} = \frac{1}{Le_1} \frac{\partial^2 c_{1v}^*}{\partial y'^2} \quad (3.49)$$

$$\frac{\partial T_2^*}{\partial t^*} = \frac{\partial^2 T_2^*}{\partial y'^2} + \dot{q}^* \quad (3.50)$$

$$\frac{\partial c_{2v}^*}{\partial t^*} = \frac{1}{Le_2} \frac{\partial^2 c_{2v}^*}{\partial y'^2} \quad (3.51)$$

with boundary conditions

$$c_{1v}^* = \epsilon \theta \quad \text{at } y = 0, -1 \quad (3.52)$$

$$T_1^* = T_2^* \frac{\partial T_1^*}{\partial y'} = \frac{\partial T_2^*}{\partial y'} \quad \text{at } y = -h^*, -(h^* + \delta^*) \quad (3.53)$$

and

$$c_{1v}^* = c_{2v}^* \frac{\partial c_{1v}^*}{\partial y'} = \frac{\partial c_{2v}^*}{\partial y'} \quad \text{at } y' = -h^*, -(h^* + \delta^*) \quad (3.54)$$

and initial conditions

$$T_1^* = T_2^* = 1 \quad \text{at } t^* = 0 \quad (3.55)$$

$$c_{1v}^* = c_{2v}^* = 0 \quad \text{at } t^* = 0$$

We next examine the magnitudes of the various dimensionless parameters so as to identify the relatively important transport mechanisms.

## 4. IDENTIFICATION OF THE IMPORTANT TRANSPORT MECHANISMS

In this section we first state the approximate range of physical properties and external conditions for typical situations of practical interest. This is followed by an estimate of the magnitudes of the dimensionless groups.

### 4.1 Physical Properties

#### Plexiglass substrate (Poly Methyl Methacrylate)

Property		Value at 378K	Range	
Density	$\rho_1$	1.19	1.0	g/cc
Specific heat	$c_{p1}$	0.37	.5	cal/g-K
Thermal conductivity	$k_1$	$5 \times 10^{-4}$	$1-10 \times 10^{-4}$	cal/cm-sec-K
Thermal conductivity	$\alpha_1$	$1.14 \times 10^{-3}$	$1-10 \times 10^{-3}$	cm <sup>2</sup> /sec
Mass diffusivity (O <sub>2</sub> )	$D_{1,v}$	$1 \times 10^{-8}$	$10^{-8}-10^{-6}$	cm <sup>2</sup> /sec

#### Air at 20°C

Thermal conductivity:	$k_g$	$0.6267 \times 10^{-4}$	cal/cm-sec-K
Thermal diffusivity:	$\alpha_g$	0.2216	cm <sup>2</sup> /sec
Mass Diffusivity (O <sub>2</sub> , N <sub>2</sub> )	$D_g$	0.2	cm <sup>2</sup> /sec

#### Electrically Conducting Layer (Indium Oxide + Stannic Oxide)

Density:	$\rho_2$	6.3	g/cc
Specific heat:	$c_{p2}$	0.2	cal/g-K
Thermal conductivity:	$k_2$	0.0136	cal/cm-sec-K

Thermal diffusivity:  $\alpha_2 = 1.08 \times 10^{-2} \text{ cm}^2/\text{sec}$

Mass diffusivity:  $D_2$  Not Available (consider:  $D_{2v}/D_{1v} = 10^{-1}, 1$  and  $10$ )

Thickness of layer:  $\delta$  typically  $1000 \text{ \AA} = 10^{-3} \text{ cm}$ , (consider:  $1 - 10 \times 10^{-3} \text{ cm}$ )

### Heats of Adsorption

The ambient temperature is taken to be  $T_\infty = 20^\circ\text{C}$  (293 K). Assuming  $Q_a = 3$  kcal/g-mole, we obtain:

$$Q_a = Q_a/RT_\infty \approx 5.2 \quad (4.1)$$

With this as an approximate estimate, a range  $Q_a = 1-25$  is considered.

Similarly, with  $Q_o \approx 1$  kcal/g-mole,  $Q_o = 1-5$  is considered.

### Heating Levels

The maximum heating levels quoted in the literature are of the order of 4 cal/cm<sup>2</sup>-sec. Therefore, the volumetric heating rating (for  $\delta = 10^{-3} \text{ cm}$ ) is

$$\dot{q}^* = \frac{\dot{q}L^2}{k_2 T_\infty} \approx 60 \quad (4.2)$$

We consider  $\dot{q}^* = 1-100$ .

### Solubility Parameter

The solubility parameter  $\epsilon$  is estimated as follows:

At the surface we have  $c_{1v} = \epsilon\theta$ . As  $\theta$  takes on large values (say, 10) the solid phase will also approach saturation ( $c_{1v} \approx 1$ ). Therefore, we take  $\epsilon = 1/10 = 0.1$ .

### Adsorption Depth

The dimensionless adsorption depth,  $H = m\sigma_0/Lc_0$  is estimated by examining the solubility of  $N_2$  in Poly Ethyl Methacrylate. At 25°C the solubility is

$$s = 7.5 \times 10^{-2} \text{ c.c. gas STP/c.c. substrate} \quad (4.3)$$

where  $s$  is defined by  $c_{1v} = sp$ . Assuming a partial pressure of  $p = 0.1 \text{ atm}$ , we find the volumetric concentration  $c_{1v}$  to be

$$c_{1v} = 7.5 \times 10^{-3} \text{ c.c. (STP)/c.c.} \quad (4.4)$$

In units of mass concentration this is

$$c_{1v} = 9 \times 10^{-6} \text{ g/c.c.} \approx 10^{-5} \text{ g/c.c.} \quad (4.5)$$

We therefore take  $c_0 \approx 10^{-5} \text{ g/c.c.}$ . If the gas is more soluble,  $c_0$  may be as large as  $10^{-3} \text{ g/c.c.}$ . For very low solubilities it may be  $10^{-7}$  or  $10^{-8} \text{ g/c.c.}$

### 4.2 Dimensionless Groups

The maximum number of available sites is of the order of  $\sigma \sim 10^{14}/\text{cm}^2$ . The parameter  $H$  is therefore given by

$$H = \frac{m\sigma_0}{Lc_0} \sim 10^{-4} \quad (4.6)$$

where  $L$  is taken to be 1 cm, and  $m = 4.67 \times 10^{-23} \text{ g}$  for  $N_2$ .

The dimensionless parameter  $\Delta$  is given by

$$\Delta = \frac{m\sigma_0 R}{L\rho_1 c_{p1}} = H \frac{c_0 R}{\rho_1 c_{p1}} = 10^{-9} \quad (4.7)$$

From these estimates it is clearly seen that surface transients ( $\theta$  terms) would be

negligibly small. Furthermore, due to the very small mass diffusivity of the solid ( $10^{-6}$  -  $10^{-7}$   $\text{cm}^2/\text{sec}$ ) compared to that in the gaseous phase (0.1  $\text{cm}^2/\text{sec}$ ), the mass transfer relationship between the surface and the ambient reduces to the quasisteady relation

$$c_{1v} = \epsilon \theta \quad (4.8)$$

where  $\theta$  is the surface coverage at the adsorption quasi-equilibrium.

The above linear relationship can be generalized by considering saturation phenomena within the solid and a Langmuir type absorption isotherm,

$$c = \frac{\epsilon \theta}{1 + \epsilon \theta} \quad (4.9)$$

can be employed.

The results of the estimates of these dimensionless groups are summarized in Table 4.1.

Table 4-1. Summary of estimate of magnitudes of dimensionless parameters

Dimensionless Parameter	Range	Comments
$Nu_t$	$O(100)$	Included in the model
$Nu_m$	$O(100)$	This is large, but irrelevant since gas-phase mass transfer does not affect problem
$\Delta$	$10^{-9}$	Negligible
$Q_o$	1-5	Included
$Q_a$	1-25	Included
$\dot{q}$	1-100	Included
$H$	$10^{-6} - 10^{-1}$	Irrelevant
$\epsilon$	$< 1$	Strongly temperature dependent. Consider values $10^{-4} - 1$
$\delta$	0.001	Consider 0.001, 0.01, 0.1
$h$	$0 < h < 1$	
$\phi_{kg}$	0.05 - 0.5	
$\phi_{Dg}$	$10^5 - 10^8$	
$Le_1$	$10^2 - 10^5$	
$\phi_{as}$	1 - 10	
$\phi_{ks}$	$10 - 100$	
$\phi_{ds}$	---	No data available, try 0.1, 1, 10

## 5. RESULTS AND DISCUSSION

The non-dimensional governing differential equations together with the simplifications discussed in §4 have been programmed for a finite-difference solution. A listing of the program is given at the end of this section. The input parameters required to run the program are also given in the listing. For the sake of clarity these parameters are listed below in the mathematical notation used in §4.

Program Notation	Mathematical Notation
DELTA	$\delta^* = \delta/L$ , thickness of heating layer
H	$h^* = h/L$ , heater location
HEAT	$\dot{q}^* = \dot{q}''L^2/kT_\infty$ , volumetric heating rate
QA	$Q_a^* = Q_a/RT_\infty$ , heats of adsorption
QO	$Q_o^* = Q_o/RT_\infty$ , heats of condensation
TINIT	$T_\infty/T_\infty = 1$ , initial temperature = ambient
CINIT	0, initial concentration in the bulk
PVBOT	$p_{v,\infty} _{-L} = p_{vL}$ , dimensionless partial pressure of vapor on the "inside" (i.e., bottom side of substrate.)
PVTOP	$p_{v,\infty} _0 = p_{v0}$ , dimensionless partial pressure of vapor on the "outside" (i.e., top side of substrate.)
ANUSTT	$Nu_{10}$ , thermal Nusselt number on the "outside"
ANUSTB	$Nu_{1L}$ , thermal Nusselt number on the "inside"
FIKG	$\phi_{kg} = k_g/k_1$ , thermal conductivity ratio (gas/plexiglass)
FIKS	$\phi_{ks} = k_2/k_1$ , thermal conductivity ratio (conductive layer/plexiglass).
FIALFS	$\phi_{as} = \alpha_2/\alpha_1$ , thermal diffusivity ratio conductive layer/plexiglass)
FIDG	$\phi_{Dg} = D_g/D_1$ , mass diffusivity ratio (gas/plexiglass)
FIDS	$\phi_{Ds} = D_2/D_1$ , mass diffusivity ratio (conductive layer/plexiglass)

ALEW1  $Le_1 = \alpha_1/D_{iv}$  Lewis number

EPS  $\epsilon = m\sigma_0/\phi c_0$  solubility parameter

The results from the various runs of the program have been plotted in Figs. 5.1-5.5.

Here we discuss each case in detail.

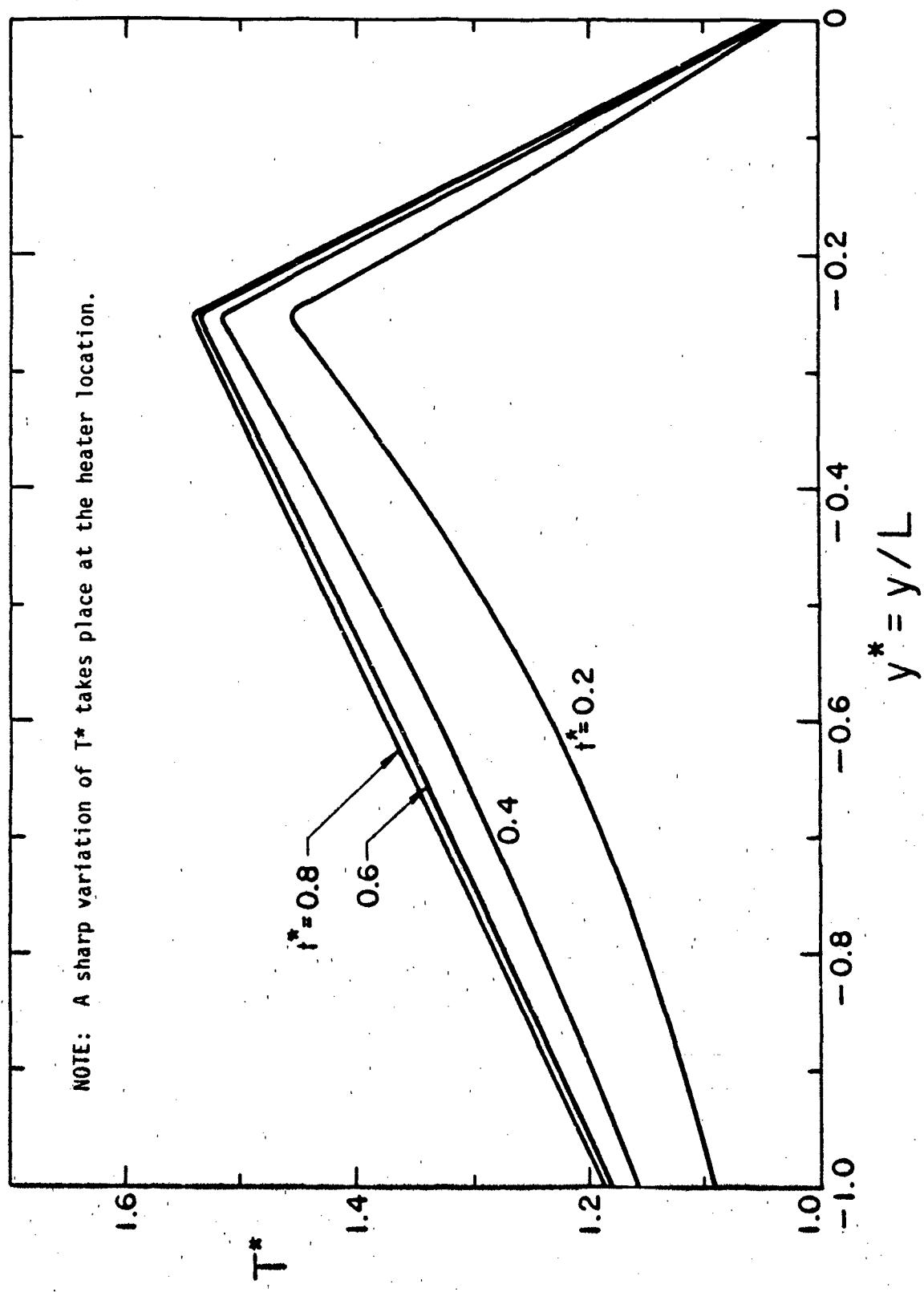
In Fig. 5.1, the temperature profile at various times is shown. The heater is placed at  $y^* = -0.25$ . The thermal parameters for this plot are  $\dot{q}^* = 50.0$ ,  $\delta^* = 0.001$ ,  $\phi_{ks} = 50.0$ ,  $Nu_{t0} = 200.0$  and  $Nu_{tL} = 10.0$ . The plot shows the following important features:

1. The region near  $y^* = 0$  reaches a steady state faster than the rest of the substrate. This is because of the higher Nusselt number and the shorter distance from the heating element.
2. More heat leaves through the surface  $y^* = 0$  than  $y^* = -1$ . This is owing to the relatively lower thermal resistance of the region  $-h^* < y^* < 0$  than  $-1 < y^* \leq -h^*$ .
3. A large Nusselt number causes the corresponding surface to be cooler and, as a result, leads to higher adsorption. The heating is therefore wasteful. If the  $Nu_t$  is controllable, then it should be minimized so that very high heating levels are not needed.
4. The maximum steady temperature in this case is  $T_{max}/T_\infty \approx 1.5$ . Assuming  $T_\infty = 300K$ , we have  $T_{max} = 450K$ . At such high temperatures the plexiglass would deteriorate.

In Fig. 5.2 the dimensionless surface coverage of the contaminant on the outside, ( $\theta_o$ ) and on the inside ( $\theta_L$ ) are shown as functions of time. The parameters for the graph are:

	H	$\delta^*$	$\phi_{ks}$	$\phi_{kg}$	$\dot{q}^*$	$Nu_{t0}$	$Nu_{tL}$	$\phi_{az}$
Run I	0.5	0.0001	10	0.05	50	200	10	1
Run II	0.25	0.001	50	0.25	50	200	10	5
Run III	0.5	0.001	50	0.25	50	10	10	5
Run IV	0.5	0.001	50	0.25	10	2	2	5

In addition we use  $Q_s = 5.0$ ,  $Q_o = 1.0$ ,  $p_{vo} = 0.5$  and  $p_{vL} = 0.01$ .



Temperature distribution within the substrate at various times

Fig. 5.1

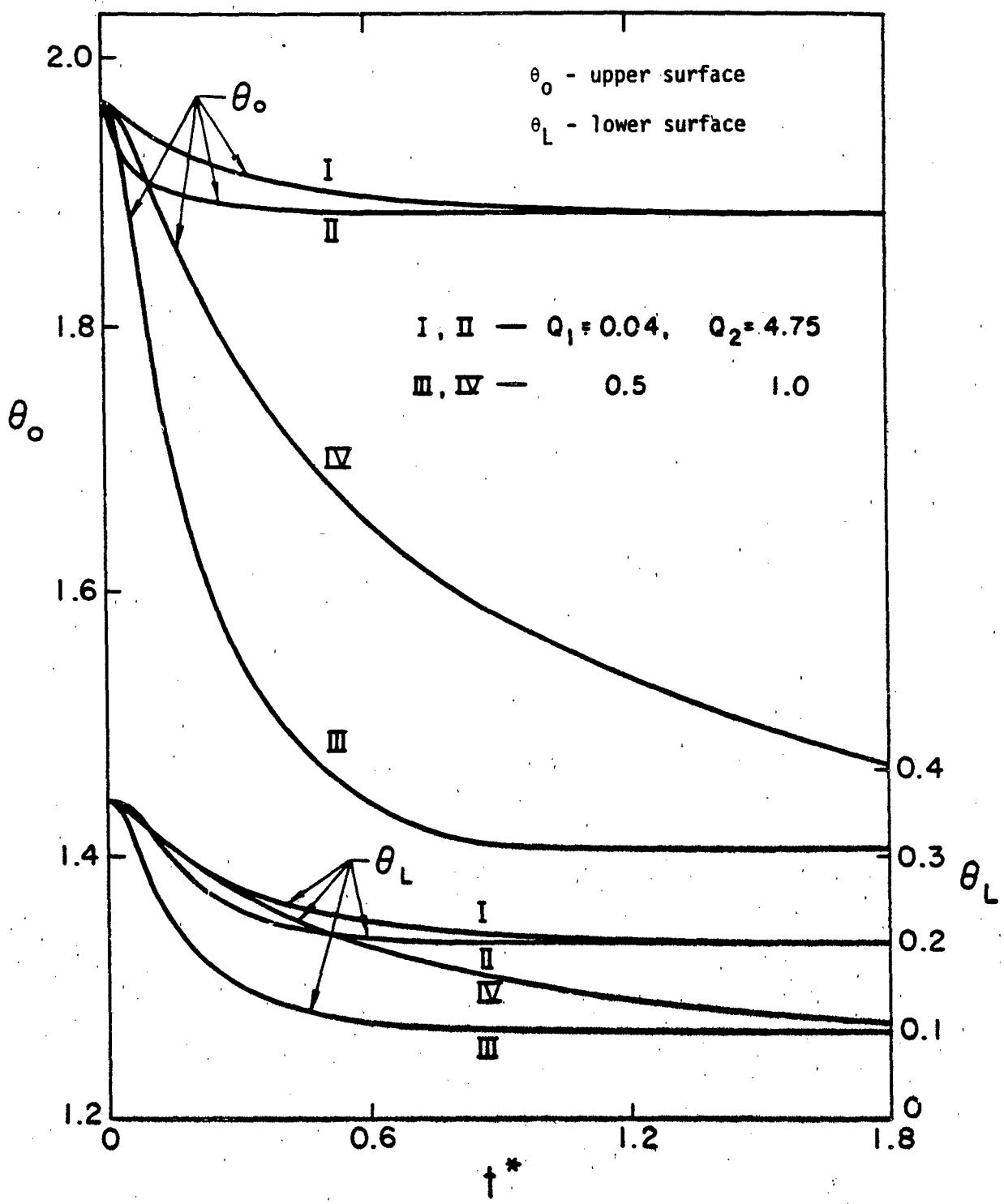


Fig. 5.2  
Dimensionless surface coverage at various times

Here we observe the following features:

1. Curves I and II, between which there is no systematic change in the thermal parameters, both reach the same steady state value for  $\theta_o$  and  $\theta_L$ . This is because the groups

$$Q_1 = \frac{1 + \text{Nu}_{to} \phi_{kg} h}{1 + \text{Nu}_{tL} \phi_{kg} (1-h)} \quad (5.1)$$

and

$$Q_2 = \frac{\dot{q}^* \delta^* \phi_{ks}}{\phi_{kg} (\text{Nu}_{to} + \text{Nu}_{tL} Q_1)} \quad (5.2)$$

have approximately the same values for these curves.

2. The curve II corresponds to a larger thermal diffusivity than curve I. It therefore approaches a steady state faster. For curve IV the Nusselt number is lower than curve III. The eigenvalues determining the rate of thermal transport are smaller for curve IV and the transport process lasts longer in this case.
3. The higher level of adsorption on the outside is due to larger partial pressure of the vapor on the outside.

In Fig. 5.3, the effects of partial pressure of the vapor and the heats of adsorption on the fraction covered are shown. The plots correspond to fixed values of the parameters  $Q_1$  and  $Q_2$  ( $Q_1 = 0.0317$ ;  $Q_2 = 11.5556$ ) or fixed values of the parameters

$$T_o = 1 + Q_2 \quad (5.3)$$

and

$$T_L = 1 + Q_1 Q_2 \quad (5.4)$$

1. We find that  $\theta_L < \theta_o$  because  $T_L > T_o$ . This is due to the convective cooling which occurs on the outside
2. Each curve shows a steep linear portion for small pressures, a flat portion for moderate pressures, and saturation ( $\theta \rightarrow \infty$ ) as the partial pressure approaches saturation.

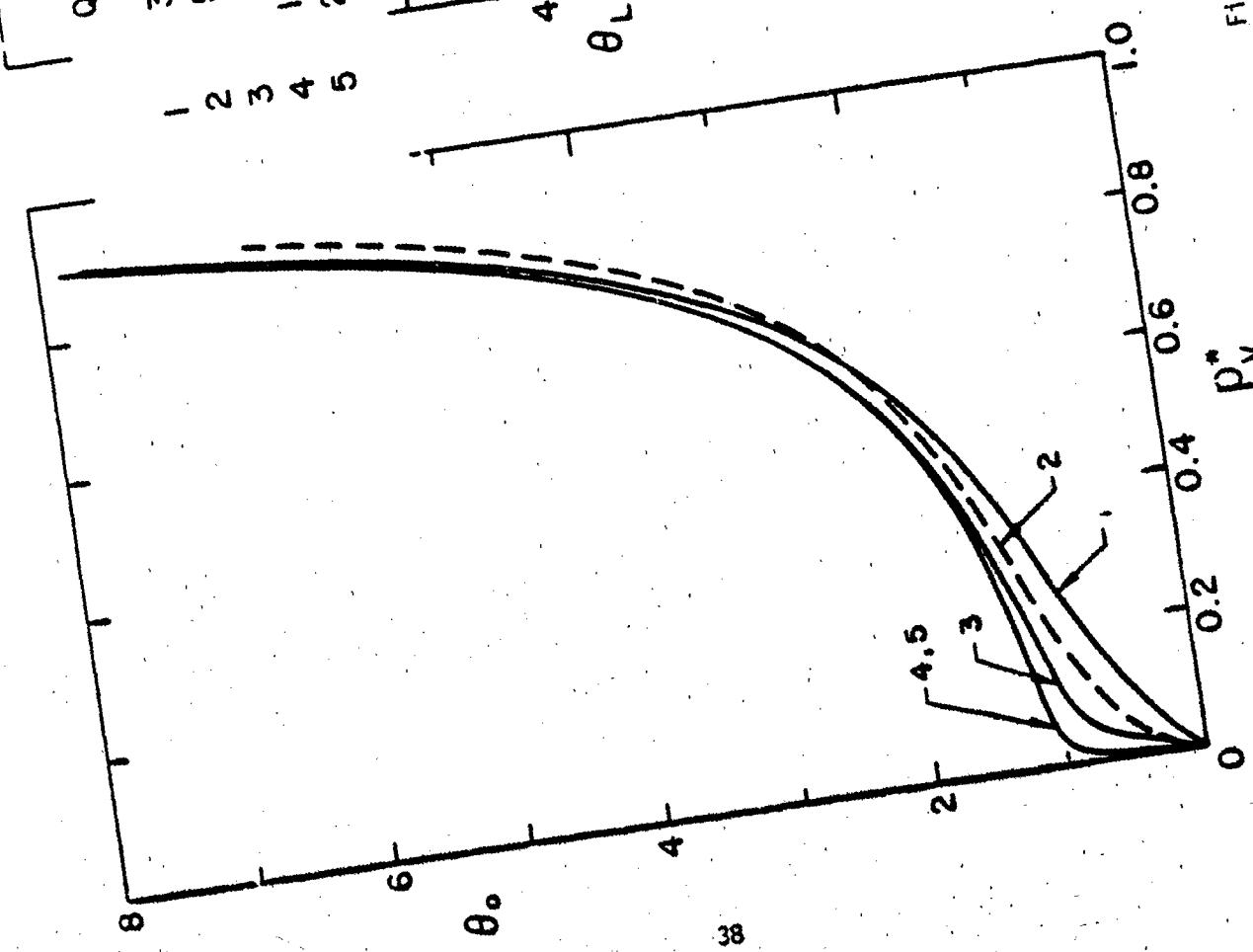
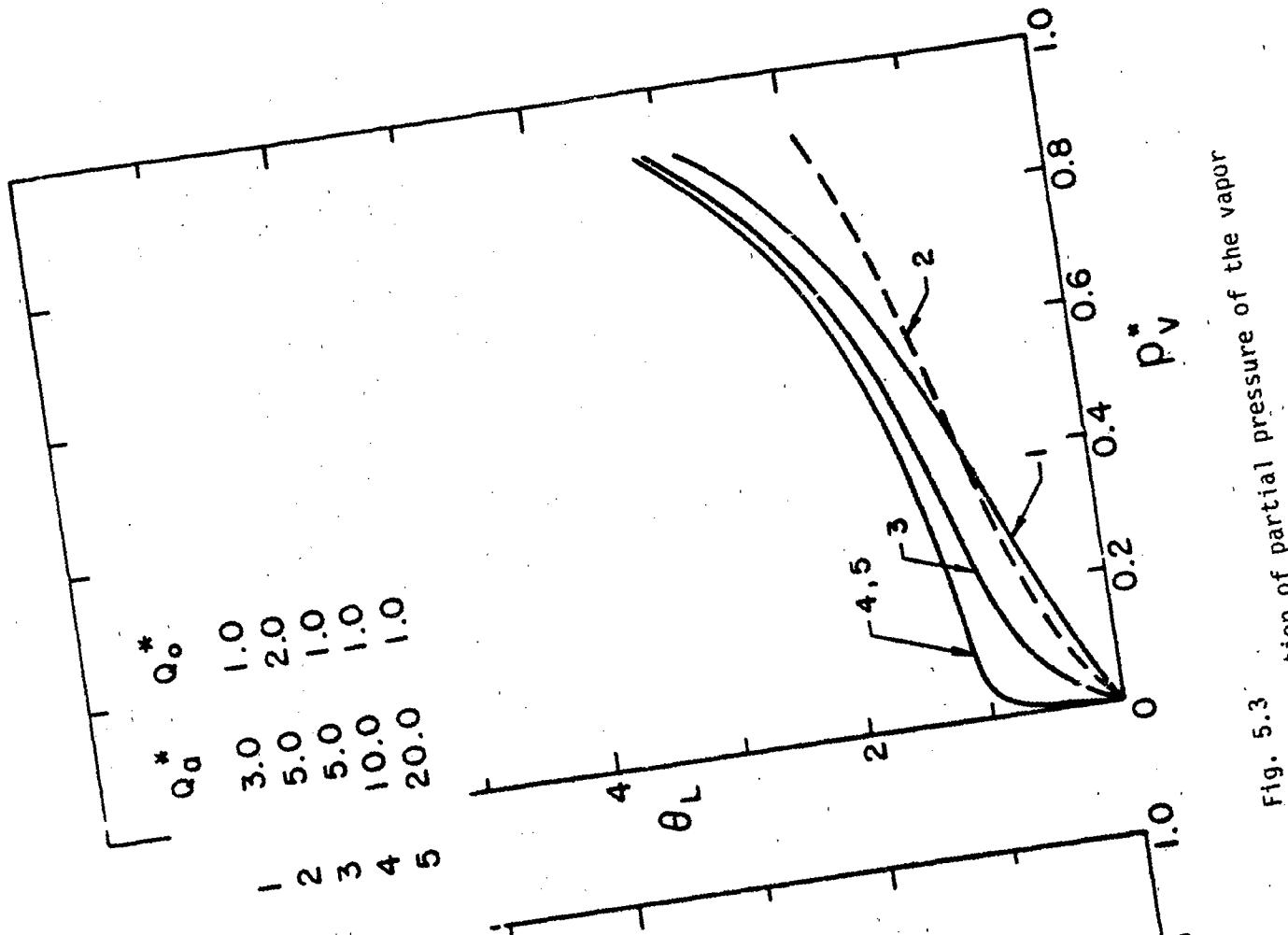


Fig. 5.3 Dimensionless surface coverage as a function of the vapor partial pressure of the vapor

3. At large  $Q_a$ , the linear and the flat portions are separated around  $\theta \sim 1$ . this implies that for large  $Q_a$  (such as in chemisorption) a monolayer is formed first until  $\theta \sim 1$ . Subsequently, more layers build up. For  $Q_a > Q_o$ , all layers may be formed simultaneously.

4. At large  $Q_o$ , the saturation phenomenon is delayed. This happens because the parameter  $k = e^{(Q_a - Q_o)/T_s}$ , which signifies the ratio of adsorption times between the first and the subsequent layers, decreases.

In Fig. 5.4, the concentration profile within the solid is plotted. The solubility has been assumed to be the same in both the substrate and the heating element. Also the ratio of the two diffusivities is taken to be unity.

The parameters are:  $L = 0.5$ ,  $\delta = 0.001$ ,  $\phi_{as} = 5.0$ ,  $\phi_{Ds} = 1.0$ ,  $\phi_{ko} = 50.0$ ,  $Le_1 = 500$ ,  $\phi_{kg} = 0.25$ ,  $\phi_{Dg} = 5.0 \times 10^5$ ,  $Q_a = 5.0$ ,  $Q_o = 1.0$ ,  $\dot{q} = 50.0$ ,  $Nu_{lo} = 10.0$ ,  $Nu_{IL} = 200.0$ ,  $\epsilon = 0.1$ ,  $p_{vo} = 0.5$  and  $q_{VL} = 0.01$ .

The plot shows:

1. The time taken to reach mass transfer steady state is approximately equal to  $Le_1 \times$  (time for thermal steady state).
2. For short times, diffusion occurs from both ends and the effects from each end grow independently until they interact.
3. As time increases, the concentration profile becomes monotonic and a straight line is obtained for constant mass diffusivity. At steady state, a steady stream of vapor diffuses from the higher concentration side to the lower concentration side.
4. The surface concentrations are given by

$$c_o = \epsilon \theta_o / (1 + \epsilon \theta_o) \quad \text{at } y = 0 \quad (5.5)$$

and

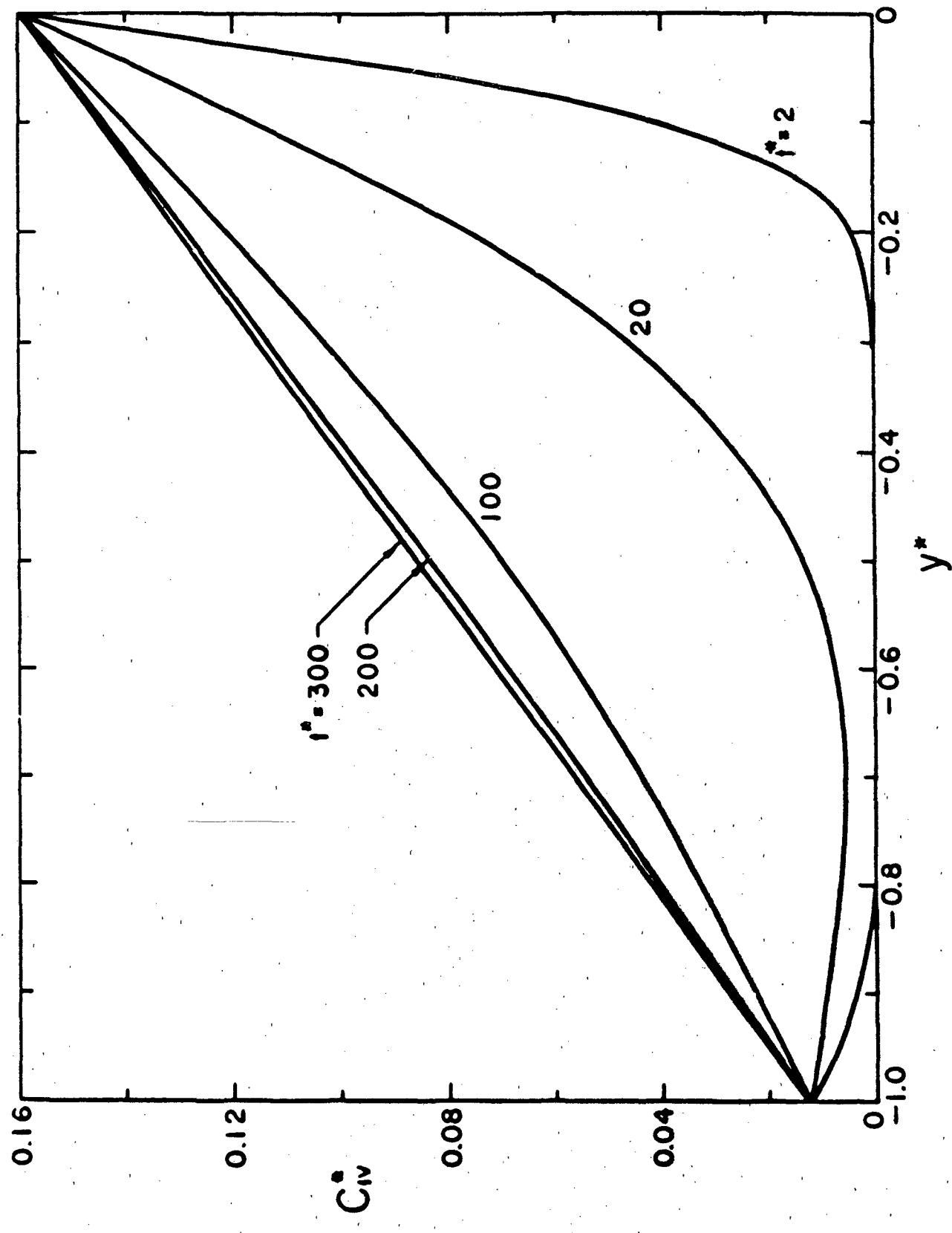


Fig. 5.4  
Volumetric concentration profile at various times

$$c_L = \epsilon \theta_L / (1 + \epsilon \theta_L) \quad \text{at } y = 1 \quad (5.6)$$

Here  $\theta_o$  and  $\theta_L$  are functions of the thermal parameters  $Q_1$  and  $Q_2$ , the heats of adsorption  $Q_a$  and  $Q_s$ , and the partial pressures  $p_{vo}$  and  $p_{vL}$ . Thus after the thermal steady state is reached,  $c_o$  and  $c_L$  remain constant due to thermal equilibrium.

In Fig. 5.5, we have plotted the variation in the steady state bulk concentration ( $c_{bulk} = \int_{-1}^0 c dy$ ) as a function of the heating rate  $\dot{q}$ . Also plotted in the same graph is  $T_{max} = T_{max}/T_\infty$  as a function of  $\dot{q}$ . The important feature incorporated here is that the solubility parameter  $\epsilon$  is taken to be temperature dependent. It is given by

$$\epsilon = \epsilon_o \theta_s^{Q_s(1-1/T_s)} \quad (5.7)$$

where  $Q_s = Q_s/RT_\infty$  is the heat of solution. Since the solubility changes with changing temperature, the heat of solution plays a role. The program was modified to include this addition parameter. The plot corresponds to the following values of the parameter:

$$\begin{array}{llll} L = 0.8, & \delta = 0.001, & \phi_{ks} = 50.0, & \phi_{kg} = 0.25, \\ Nu_{to} = 200.0, & Nu_{tL} = 100. & \epsilon_o = 0.1, & Q_s = 10.0, \\ Q_o = 1.0, & p_{vo} = 0.5, & p_{vL} = 0.01, & Q_s = 0.0-1.0. \end{array}$$

The results exhibit the following features:

1. For very low heat of solution,  $Q_s$ , the bulk concentration decreases monotonically with the heating level  $\dot{q}$ . It may be noted that the duration of heating does not determine the level of contamination after the attainment of thermal and mass transfer steady states. For this reason the level of initial contamination or the initial temperature do not affect  $c_{bulk}$ .
2. For a reasonably large heat of solution, while the surface coverage ( $\theta_o$  and  $\theta_L$ ) decreases with increasing temperature, the dissolved contaminant in the bulk increases. This usually happens when the heating levels are low and the change of  $\theta_o$  and  $\theta_L$  are not as rapid as that of the solubility. If the outside environment is very cold and if the convective cooling is strong, the interior of the substrate may be very hot, but the surface will remain fairly cool. As a result, the heating may not substantially remove the surface contaminant and

NOTE: For  $Q_s^* = 0.1-0.5$ , an increase in heating level  $q^*$  from 0 to about 25 actually increases in the contaminant level in the steady state.

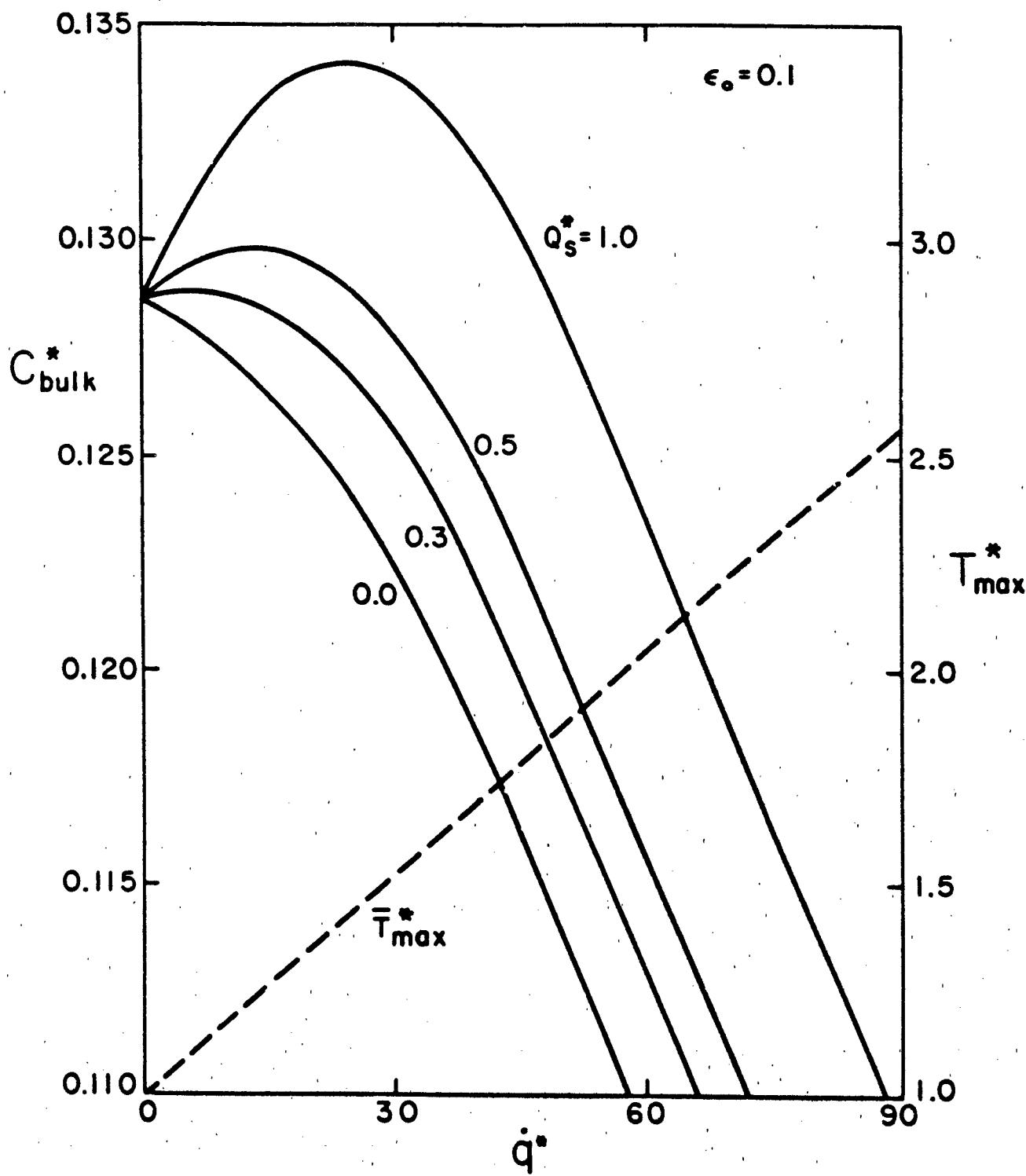


Fig. 5.5

Steady state average volumetric concentration  $c_{bulk}^*$  and maximum temperature,  $T_{max}^*$ , as function of heating level  $q^*$ .

at the same time it will increase the solubility. This will lead to increased contamination if heating is sustained for long periods.

3. An important consideration for design would be the maximum temperature reached:

$$T_{\max} = \frac{T_{\infty} + T_L h^* / (1-h^*) + \dot{q} \delta h^* \phi_{ks}}{1 + h^* / (1-h^*)} \quad (5.7)$$

If  $T_{\infty} \approx 300K$ , then for a material such as plexiglass, we would require  $T_{\max} \leq 1.5$  to avoid thermal damage.

## 6. RECOMMENDATIONS AND CONCLUDING REMARKS

Here we further discuss the feasibility of decontamination by heating and the limitation of the effectiveness. We also make recommendations for experimental measurements for obtaining the required data in order to run the computer code. In addition, we make several recommendations so that all of the important physical phenomena may be incorporated into the computer program, and that concrete design criteria may be established for engineering use.

### 6.1 Recommendations for Experiments

The required dimensionless parameters are all given in §5. Most of the data needed to calculate these parameters are available except for some information on adsorption/desorption kinetics and thermal permeability of the solid substrate. In particular, the following measurements are required:

- a. Adsorption Isotherm: The functional dependence of the heat of adsorption on the temperature [i.e.,  $Q(T)$ ] is a necessary parameter. For this measurement we may take a solid sample and heat it up in order to remove all contaminants. Then at a given partial pressure of the contaminant, expose it for a short period of time (say, 2-3 minutes) while holding its temperature fixed at  $T$ . By subsequently reheating the sample and measuring the volume of gaseous contaminant that desorbs, the surface coverage  $\theta$  may be calculated. Then we could calculate the constant using  $x = p/p_0$ . By using (2.32) and noting that  $Q_0$  is approximated to be the latent heat of condensation,  $Q_0$  can be found. Equation (2.37) then yields the value of  $Q$ .
- b. Permeability: The mass diffusion coefficient,  $D_{1v}$ , and the maximum solubility  $c_0$  are the other physical properties that have to be measured at various temperatures. For this measurement one should take a thin sheet of the uncontaminated (or decontaminated) substrate and expose it to a contaminant on one side. By letting the contaminant penetrate to the other side and measuring the concentration profile as a function of time one may calculate the diffusion coefficient. When the substrate saturates, the maximum concentration  $c_0$  may be calculated.

## **6.2 Recommendations for Further Work**

The present analysis is based on one-dimensional heat and mass diffusion in the substrate having constant physical properties. Only a simple variation of the solubility with temperature has been treated (Fig. 5.5) for the purpose of examination of adverse effects of heating. Since many of the other properties are held constant the accuracy is likely to be poor. In order to establish design criteria for quantities such as optimal heating rate or for optimal heater location further work is clearly necessary. We recommend the following:

- i. Complete Variable Property Analysis: The mass diffusivity, vapor solubility and the heats of adsorption have to be considered as functions of temperature. As noted earlier, property variations can cause the decontamination system to be not only ineffective, but counterproductive.
- ii. Multi-Element Optimal Heating: For thick substrates, a great deal of heating may be necessary in order to achieve the required surface temperature. This can cause heat damage as well as contamination due to increased solubility. The solution to the problem includes the possibility of having two or more elements in order to have a more even distribution of heat. Optimal positioning in this case would be quite important especially if the desorption characteristics are different on each of the two sides of the substrate.
- iii. Multicomponent Adsorption: The current theory only deals with a single component of contaminant vapor. In real situations two or more different species of vapor may be present. A generalization to account for this is needed.
- iv. Chemisorption and Chemical Reactions: The model developed so far only takes care of physical adsorption. Various modifications are necessary in order to deal with chemical adsorption. Also, there may be some important effects due to chemical reaction in the bulk of the substrate.
- v. Two-Dimensional Analysis: Our one-dimensional analysis utilizes constant average transport parameters in the gaseous phase ( $Nu$ ). For practical circumstances the momentum and the thermal boundary layer thicknesses vary along the surface of the substrate. Further modification to allow for this is required.

### **6.3 Conclusions**

With a complete analysis as recommended accurate design criteria can be established on a sound scientific basis. A high degree of accuracy may be necessary for some critical cases for which heating levels may have to be pushed to the maximum limits. As noted in items (i) and (ii) careful design is needed for substrates exposed to certain extreme conditions under which heating may actually increase the contaminant level. It is also clear from this study that heating can be used to preclude a substrate from being contaminated. Here again the optimal heating levels for various external circumstances need to be established on the basis of practical considerations.

In closing, we affirm that there is definite merit in conductive film heating for decontamination or for precluding contamination. With the acquisition of recommended data and with further generalization of the computer code, workable systems may be designed with the least possible experimentation.

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## GLOSSARY

$c_v$	-	concentration of absorbed vapor within the solid
$c_o$	-	maximum vapor concentration that is dissolvable in the solid (This is related to the available absorption sites per unit volume)
$c_p$	-	specific heat
$D$	-	mass diffusion of vapor (in ambient gas or solid)
$h$	-	heater depth from outside surface
$H$	-	dimensionless adsorption depth [equation (3.28)]
$k$	-	thermal conductivity
$L$	-	thickness of the slab
$Le$	-	Lewis number ( $= \alpha/D$ )
$m$	-	mole fraction of the contaminant vapor molecules
$Nu$	-	Nusselt number
$p_v$	-	partial pressure of vapor
$\dot{q}$	-	volumetric heating rate
$Q_a$	-	molar heat of adsorption for the first layer of adsorbed molecules
$Q_o$	-	molar heat of condensation
$Q_s$	-	molar heat of solution
$R$	-	universal gas constant
$t$	-	time
$T$	-	temperature

$T_s$	-	surface temperature
$T_\infty$	-	ambient temperature
$x$	-	dimensionless partial pressure (also equal to mole fraction)
$y$	-	coordinate normal to the slab

#### Greek Letters

$\alpha$	-	thermal diffusivity
$\delta$	-	thickness of heating element
$\Delta$	-	coupling parameter governing the thermal transients of the slab surface [Equation (3.27)]
$\epsilon$	-	solubility parameter which links surface coverage and bulk concentration at the surface [ $c = \epsilon \theta / (1 + \epsilon \theta)$ ].

$\phi$	-	property ratio
$\delta$	-	density
$\sigma$	-	dimensional surface coverage
$\sigma_0$	-	available adsorption sites per unit area
$\theta$	-	dimensionless surface coverage ( $= \sigma / \sigma_0$ )

#### Subscripts

$0$	-	upper surface
$1$	-	substrate material (plexi-glass)
$2$	-	heater material (Indium-Tin Oxide)
$\infty$	-	Ambient far-stream quantity
$D$	-	mass diffusivity ratio
$g$	-	for property of gas-vapor mixture
$k$	-	thermal conductivity ratio

- L** - lower surface
- m** - mass transfer
- s** - at the slab surface; property ratio between solids 2 and 1
- t** - thermal
- v** - contaminant vapor
- $\alpha$**  - thermal diffusivity ratio

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## APPENDIX

PROGRAM TO SOLVE FOR THE DIFFUSION OF HEAT AND  
CONTAMINANT VAPOR WITHIN A SOLID-SUBSTRATE WITH AN  
IMBEDDED CONDUCTIVE LAYER

BLANK

C\*  
 C\*  
 C\* THIS PROGRAM SOLVES FOR THE DIFFUSION OF HEAT AND CONTAMINANT  
 C\* VAPOR WITHIN A SOLID-SUBSTRATE (PLEXI-GLASS) WITH AN EMBEDDED  
 C\* CONDUCTIVE LAYER ( INDIUM-TIN OXIDE). THE NUMERICAL PROCEDURE  
 C\* IS BASED ON THE IMPLICIT FINITE DIFFERENCE PROCEDURE. THE  
 C\* PROGRAM IS CURRENTLY SET FOR A MAXIMUM OF 1000 INTERVALS FOR  
 C\* SPACIAL DIFFERENCING. IF 'N' IS THE NUMBER OF INTERVALS REQUIRED  
 C\* THE ARRAYS HAVE TO BE DIMENSIONED AS 'N+1'.  
 C\*\*  
 C\*\*  
 C\*\* THE INPUTS TO THE PROGRAM ARE:  
 C\*\*  
 C\*\* NR,NW - DEVICE NUMBERS FOR READING DATA AND WRITING  
 C\*\* OUTPUT. THESE ARE SPECIFIED THROUGH THE DATA  
 C\*\* STATEMENT IN THE BEGINNING OF THE PROGRAM.  
 C\*\* MAXSTP - MAXIMUM NUMBER OF TIME STEPS  
 C\*\* ILIST - NUMBER OF TIME STEPS AFTER WHICH SURFACE  
 C\*\* TEMPERATURE AND CONCENTRATION AND INTEGRATED  
 C\*\* BULK CONCENTRATION WILL BE PRINTED.  
 C\*\* IGRID1 - NUMBER OF GRID SPACES BETWEEN THE HEATER AND  
 C\*\* INSIDE SURFACE  
 C\*\* IGRID2 - NUMBER OF GRID SPACES IN THE HEATING LAYER  
 C\*\* IGRID3 - NUMBER OF GRID SPACES BETWEEN THE OUTSIDE  
 C\*\* SURFACE AND THE HEATING LAYER  
 C\*\* IPROF - NUMBER OF TIME STEPS AFTER WHICH TEMPERATURE  
 C\*\* AND CONCENTRATION PROFILES ARE REQUIRED  
 C\*\* DELTA - THICKNESS OF HEATING LAYER  
 C\*\* H - DEPTH AT WHICH HEATER IS LOCATED  
 C\*\* DT - TIME STEP; FOR STUDY OF THERMAL TRANSIENTS A  
 C\*\* TIME STEP OF 1/MAXSTP IS RECOMMENDED. FOR THE  
 C\*\* STUDY OF MASS TRANSIENTS WITHIN THE SOLID, A  
 C\*\* TIME STEP OF (LEWIS #)/MAXSTP IS RECOMMENDED.  
 C\*\* HEAT - DIMENSIONLESS,VOLUMETRIC HEATING LEVEL  
 C\*\* QA - DIMENSIONLESS HEAT OF ADSORPTION  
 C\*\* QO - DIMENSIONLESS HEAT OF CONDENSATION  
 C\*\* TINIT - DIMENSIONLESS INITIAL TEMPERATURE  
 C\*\* CINIT - DIMENSIONLESS INITIAL CONCENTRATION  
 C\*\* PVBOT - DIMENSIONLESS PARTIAL PRESSURE OF VAPOR ON  
 C\*\* THE INSIDE  
 C\*\* PVTOP - DIMENSIONLESS PARTIAL PRESSURE OF VAPOR ON  
 C\*\* THE OUTSIDE  
 C\*\* ANUSTT - THERMAL NUSSELT NUMBER ON OUTSIDE  
 C\*\* ANUSTB - THERMAL NUSSELT NUMBER ON INSIDE  
 C\*\*\*  
 C\*\*\* FIKG - THERMAL CONDUCTIVITY RATIO (GAS/PL. GLASS)  
 C\*\*\* FIKS - THERMAL CONDUCTIVITY RATIO (COND. LAYER/PL. GLASS)  
 C\*\*\* FIALFS - THERMAL DIFFUSIVITY RATIO (COND. LAYER/PL.GLASS)  
 C\*\*\* FIDG - MASS DIFFUSIVITY RATIO(GAS/PL. GLASS)  
 C\*\*\* FIDS - MASS DIFFUSIVITY RATIO(COND. LAYER/PL. GLASS)  
 C\*\*\* ALEW1 - LEWIS NUMBER OF PLEXI-GLASS  
 C\*\*\* EPS - SOLUBILITY PARAMETER

```

C*
C*      THE GIVEN INPUT DATA IS PRINTED OUT. HERE 'NW' REFERS
C*      TO THE OUTPUT DEVICE NUMBER.
C*
      WRITE(NW,300) IMAX,H,DELTA,DT
      WRITE(NW,301) FIALFS,FIDS,FIKS,ALEW1,FIKG,FIDG
      WRITE(NW,302) QA,QQ,HEAT
      WRITE(NW,303) ANUSTB,ANUSTT
      WRITE(NW,304) EPS
      WRITE(NW,305) TINIT,CINIT,PVBOT,PVTOP
300   FORMAT(10X,'NUMBER OF GRID PTS = ',I5/,10X,'DEPTH OF HEATER = ',
*F8.5/,10X,'THICKNESS OF HEATED LAYER = ',F8.5/,10X,
*TIME STEP = ',F8.5//)
301   FORMAT(10X,'THERMAL DIFFUSIVITY RATIO (S2/S1) = ',F10.5/,10X,
*MASS DIFFUSIVITY RATIO (S2/S1) = ',F10.5/,10X,'THERMAL '
*,CONDUCTIVITY RATIO (S2/S1) = ',F10.5/,10X,'LEWIS NUMBER
* OF SOLID 1 = ',D12.4/,10X,'THERMAL CONDUCTIVITY RATIO (G/S1)= '
*,D12.4/,10X,'MASS DIFFUSIVITY RATIO (G/S1) = ',D12.4//)
302   FORMAT(10X,'HEAT OF ADSORPTION = ',F10.5,10X,'HEAT OF'
*,CONDENSATION = ',F10.5/,10X,'HEATING RATE = ',F10.5//)
303   FORMAT(10X,'NUSSELT NUMBER (THERMAL) ON INSIDE = ',F10.5/
*,10X,'NUSSELT NUMBER (THERMAL) ON OUTSIDE = ',F10.5//)
304   FORMAT(10X,'PARAMETER EPSILON = ',D12.4//)
305   FORMAT(10X,'INITIAL TEMP = ',F10.5,10X,'INITIAL CONC = ',F12.8/
*10X,'VAPOR FRACTION INSIDE = ',F10.5,10X,'VAPOR FRACTION',
*' OUTSIDE = ',F10.5//)
C**
C**      INITIAL CONDITIONS ARE SPECIFIED.
C**
      DO 1 I=1,IMAX
      QTH(I) = 0.0
      QD(I) = 0.0
      C(I) = CINIT
1      T(I) = TINIT
      DO 2 I=IHLOW,IHUP
      2      QTH(I) = HEAT
C***      THE COEFFICIENTS FOR THE TRI-DIAGONAL FINITE DIFFERENCE
C***      EQUATIONS ARE CALCULATED.
C***
      FIALF1 = 1.0
      FIALF2 = FIALFS
      FID1 = 1.0/ALEW1
      FID2 = FIDS/ALEW1
      C1 = DT/(DY1*DY1)
      C2 = DT/(DY2*DY2)
      C3 = DT/(DY3*DY3)
      BM1 = C1*FID1
      BM2 = C2*FID2
      BM3 = C3*FID1
      FIMK = FIDS
      GMB = AMB/FID1 + AMB*AMB*FIMK/FID2
      GMT = AMT/FID1 + AMT*AMT*FIMK/FID2
      BT1 = C1*FIALF1
      BT2 = C2*FIALF2
      HT3 = C3*FIALF1
      FITK = FIKS
      GTB = AMB/FIALF1 + AMB*AMB*FITK/FIALF2
      GTT = AMT/FIALF1 + AMT*AMT*FITK/FIALF2
      CALL COEFM(BM1,BM2,BM3,FIMK,GMB,GMT,SUBM,DIAM,SUPM)
      CALL COEFM(BT1,HT2,BT3,FITK,GTB,GTt,SUBT,DIAT,SURT)

```

```

IMPLICIT REAL*8(A-H,O-Z)
DIMENSION QTH(1001),QD(1001),T(1001),C(1001),Y(1001)
DIMENSION SUBM(1001),DIAM(1001),SUPM(1001),BM(1001)
DIMENSION SUBT(1001),DIAT(1001),SUPT(1001),BT(1001)
DIMENSION DIT(1001),DIM(1001)
DIMENSION TEMC1(1001),TEMC2(1001),TEMC3(1001)
COMMON/AREA2/IMAX,IHLOW,IHUP,DY1,DY2,DY3,AMB,AMT,DT
COMMON /AREA1/QA,Q0
DATA NR/5/,NW/6/

C*
C* INPUT DATA TO BE PROVIDED FOR THE PROGRAM. IN THE READ
C* STATEMENTS 'NR' REFERS TO THE INPUT DEVICE NUMBER.
C*
      READ(NR,99) MAXSTP,ILIST
      READ(NR,99) IGRID1,IGRID2
      READ(NR,99) IGRID3,IPROF
      READ(NR,100) DELTA,H,DT
      READ(NR,100) HEAT,QA,Q0
      READ(NR,101) TINIT,CINIT,PUTOP,PUBOT
      READ(NR,101) ANUSTT,ANUSTB
      READ(NR,102) FIKG,FIKS,FIALFS
      READ(NR,102) FIDG,FIDS,ALEW1
      READ(NR,102) EPS
99      FORMAT(2I5)
100     FORMAT(3F20.9)
101     FORMAT(4F10.5)
102     FORMAT(3X,D9.2,3X,D9.2,3X,D9.2)
C*** C*** SAMPLE DATA - (THE FIRST AND LAST LINES HERE INDICATE THE
C*** C*** COLUMN NUMBERS. THESE ARE TO BE OMITTED IN
C*** C*** THE ACTUAL DATA.)
C*** C*** 12345678901234567890123456789012345678901234567890
C*** C*** 4000 100
C*** 50 10
C*** 50 1000
C*** 0.001 0.50 0.0002
C*** 50.000 5.00 1.0
C*** 1.0 0.0 0.5 0.01
C*** 200.0 10.0
C*** 0.25D+000 5.00D+001 0.50D+001
C*** 1.00D+007 0.10D+001 1.00D+004
C*** 1.00D-001
C*** C*** 12345678901234567890123456789012345678901234567890
C*** C*** C*
C*      CREATION OF THE FINITE DIFFERENCE GRID
C*
      CALL GRID(IGRID1,IGRID2,IGRID3,H,DELTA,Y)
C*
C*

```

```

C**
C*      THE LOOP FOR CALCULATING QUANTITIES AT NEW TIME LEVEL.
C**

      ITIME = 0
      TIME = 0.0
      TLOLD = TINIT
      TUPOLD= TINIT
      XLOLD = PVBOT
      XUPOLD= PVTOP
      IPRINT = 0
1000  ITIME = ITIME + 1
      IF(ITIME .GT. MAXSTP) GO TO 1001
      TIME = TIME + DT
      TLOW = T(1)
      TUP = T(IMAX)

C*      NEW VALUE OF THE SURFACE COVERAGE (THETA) IS CALCULATED.
C*
      CALL CALX(TLOLD,TLOW,XLOLD,XLOW)
      CALL CALX(TUPOLD,TUP,XUPOLD,XUP)
      CALL CALHTH(TLOW,XLOW,THETLO)
      CALL CALHTH(TUP,XUP,THETUP)

C*      TLOLD = TLOW
      TUPOLD= TUP
      XLOLD = XLOW
      XUPOLD= XUP
      IPRINT = IPRINT + 1
      ICHEK = IPRINT/ILIST
      IF(IPRINT .NE. (ICHEK*ILIST)) GO TO 555
      WRITE(NW,149) TIME
      WRITE(NW,160)
160   FORMAT(5X,'TEMP IN',5X,'THETA IN')
      WRITE(NW,150) TLOW,THETLO
      WRITE(NW,161)
161   FORMAT(5X,'TEMP OUT',5X,'THETA OUT')
      WRITE(NW,150) TUP,THETUP

C*      THE BULK CONCENTRATION OF VAPOR IN THE SOLID IS CALCULATED
C*      USING SIMSON'S RULE INTEGRATION.
C*
      DO 330 I=1,IHLOW
330   TEMC1(I) = C(I)
      DO 331 I=IHLOW,IHUP
331   TEMC2(I-IGRID1) = C(I)
      DO 332 I=IHUP,IMAX
332   TEMC3(I-IGRID1-IGRID2) = C(I)
      I1 = IHLOW
      I2 = IGRID2 + 1
      I3 = IHLOW
      CALL SIMRUL(I1,TEMC1,DY1,CB1)
      CALL SIMRUL(I2,TEMC2,DY2,CB2)
      CALL SIMRUL(I3,TEMC3,DY3,CB3)
      CBULK = CB1 + CB2 + CB3
      WRITE(NW,163) CBULK
163   FORMAT(10X,'CBULK = ',F14.8,/)
C**

```

```

C*
C*      THE CONCENTRATION AND TEMPERATURE PROFILES ARE PRINTED
C*      ALONG WITH THE VALUE OF THE Y- COORDINATE.
C*
161      ICHEK = IPRINT/IPROF
162      IF(IPRINT .NE. (ICHEK*IPROF) ) GO TO 555
163      WRITE(NW,162)
164      FORMAT(5X,'CONC.',8X,'TEMP.',10X,'Y COORD.'//)
165      WRITE(NW,200) (C(I),T(I),Y(I),I=1,IMAX)
166      FORMAT(//10X,'TIME = ',F12.8//)
167      FORMAT(3F14.6//)

C***      INCORPORATION OF THE HEAT TRANSFER BOUNDARY CONDITIONS
C***      AT THE OUTSIDE AND INSIDE SURFACES.
C***      CALL TBOUND(1,DY1,SUBT,DIAT,SUPT,TLOW,XLOW,ANUSTB,FIKG,DEL)
C***      CALL TBOUND(IMAX,DY3,SUBT,DIAT,SUPT,TUP,XUP,ANUSTT,FIK3,DEL)
C***      CALL SOURCE(BT1,BT2,BT3,FITK,GTB,GTt,T,QTH,BT)
C***      BT(1) = T(1) + DIAT(1) - 1 + SUPT(1)
C***      BT(IMAX) = T(IMAX) + DIAT(IMAX) - 1. + SUBT(IMAX)

C***      INCORPORATION OF THE SOLUBILITY CONDITIONS FOR VAPOR
C***      DIFFUSION INTO THE SOLID.
C***      CALL SOURCE(BM1,BM2,BM3,FIMK,GMB,GMT,C,QA,BM)
C***      DUM1 = EPS*THETLO
C***      BM(1) = DUM1/(1.+ DUM1)
C***      DUM2 = EPS*THETUP
C***      BM(IMAX) = DUM2/(1.+DUM2)

C**      THE TRI-DIAGONAL MATRIX INVERSION PROCEDURE FOR UPDATING
C**      THE TEMPERATURE AND CONCENTRATION SOLUTIONS AT EACH TIME
C**      LEVEL.
C**      DO 20 I=1,IMAX
C**      DIT(I) = DIAT(I)
20      DIM(I) = DIAM(I)
C**      CALL TRID(SUBM,DIM,SUPM,BM,IMAX)
C**      CALL TRID(SUBT,DIT,SUPT,BT,IMAX)
C**      DO 21 I=1,IMAX
C**      C(I) = BM(I)
C**      T(I) = BT(I)
21      CONTINUE
C**      GO TO 1000
200     FORMAT(3F15.8)
1001    STOP
C**      END

C**
C**
C**
C**

```

```

*****
**** THIS SUBROUTINE COMPUTES THE RIGHT-HAND SIDE VECTOR FOR
**** TRI-DIAGONAL MATRIX INVERSION PROCEDURE. THE TERM
**** INVOLVES TEMPERATURE (OR CONCENTRATION) AT OLD TIME
**** LEVEL AND ALSO THE VOLUMETRIC SOURCE FOR HEAT OR MASS.
****

SUBROUTINE SOURCE(BM1,BM2,BM3,FIMK,GMB,GMT,C,QA,BM)
IMPLICIT REAL*8(A-H,O-Z)
COMMON/AREA2/IMAX,IHLOW,IHUP,DY1,DY2,DY3,AMB,AMT,DT
DIMENSION QA(1001),BM(1001),C(1001)
DO 10 I=1,IHLOW
BM(I) = C(I) + BM1*DY1*DY1*QA(I)
10 CONTINUE
DO 11 I=IHLOW,IHUP
BM(I) = C(I) + BM2*DY2*DY2*QA(I)
11 CONTINUE
DO 12 I=IHUP,IMAX
BM(I) = C(I) + BM3*DY3*DY3*QA(I)
12 CONTINUE
BM(IHLOW) = C(IHLOW) + DT*AMB*AMB*FIMK*QA(IHLOW)/GMB
BM(IHUP) = C(IHUP) + DT*AMT*AMT*FIMK*QA(IHUP)/GMT
RETURN
END

*****
*****

```

```

*****
**** THIS SUBROUTINE INCORPORATES THE HEAT TRANSFER BOUNDARY
**** CONDITIONS ON THE OUTSIDE AND INSIDE SURFACES.
****

SUBROUTINE TBOUND(I,DY,SUBT,DIAT,SUPT,TS,XS,ANUST,FIKG,DEL)
IMPLICIT REAL*8(A-H,O-Z)
COMMON/AREA2/IMAX,IHLOW,IHUP,DY1,DY2,DY3,AMB,AMT,DT
COMMON /AREA1/QA,QA
DIMENSION SUBT(1001),DIAT(1001),SUPT(1001)
CALL THETAP(TS,XS,DERIV)
F1 = ANUST*FIKG
F2 = DEL*DERIV*( QA + (QA-QA)*(1.-XS) )
DUM1= DT/(0.5*DY*DY - F2*DY )
DUM2= (1.+F1*DY)*DUM1
DIAT(I) = 1. + DUM2
SUBT(I) = -DUM1
SUPT(I) = -DUM1
RETURN
END

*****

```

C\*\*\*  
C\*\*\* THIS SUBROUTINE GENERATES THE SPACIAL GRID FOR THE  
C\*\*\* FINITE DIFFERENCE PROCEDURE.  
C\*\*\*

```
SUBROUTINE GRID(IGRID1,IGRID2,IGRID3,H,DELTA,Y)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION Y(1001)
COMMON/AREA2/IMAX,IHLOW,IHUP,DY1,DY2,DY3,AMB,AMT,DT
IMAX = IGRID1 + IGRID2 + IGRID3 + 1
IMAX1 = IMAX - 1
IHLOW = IGRID1 + 1
IHUP = IHLOW + IGRID2
DY1 = (1. - H - DELTA)/DFLOAT(IGRID1)
DY2 = DELTA/DFLOAT(IGRID2)
DY3 = H/DFLOAT(IGRID3)
AMB = DY2/DY1
AMT = DY2/DY3
Y(1) = -1.0
DO 1 I=2,IHLOW
1 Y(I) = Y(I-1) + DY1
DO 2 I=1,IGRID2
2 Y(IHLOW + I) = Y(IHLOW + I - 1) + DY2
DO 3 I=IHUP,IMAX1
3 Y(I+1) = Y(I) + DY3
RETURN
END
```

C\*\*\*  
C\*\*\*

C\*\*  
C\*\* THIS SUBROUTINE CALCULATES THE EXTENT OF SURFACE COVERAGE
C\*\* (THETA) AS A FUNCTION OF TEMPERATURE AND DIMENSIONLESS
C\*\* PARTIAL PRESSURE.  
C\*\*

```
SUBROUTINE CALHT(TS,X,THETA)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /AREA1/QA,Q0
DUM1 = (QA - Q0)/TS
CONS = DEXP(DUM1)
DUM2 = (1.-X)*(1. - X + CONS*X)
THETA= CONS*X/DUM2
RETURN
END
```

C\*\*  
C\*\*

C\*\*\*  
C\*\*\* THIS SUBROUTINE CALCULATES THE NEW DIMENSIONLESS PARTIAL
C\*\*\* PRESSURE AT THE NEW TEMPERATURE.  
C\*\*\*

```
SUBROUTINE CALX(TSOLD,TSNEW,XOLD,XNEW)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /AREA1/QA,Q0
POW = -Q0*( 1./TSOLD - 1./TSNEW)
XNEW = XOLD*DEXP(POW)
RETURN
END
```

C\*\*\*  
C\*\*\*

```
***  
*** THIS SUBROUTINE SOLVES FOR A SYSTEM OF EQUATIONS OF THE  
*** FORM [A]3*[X]3 = [B]3, WHERE THE MATRIX [A]3 IS TRI-DIAGONAL.  
***
```

```
SUBROUTINE TRID(SUB,DIAG,SUP,B,N)  
IMPLICIT REAL*8(A-H,O-Z)  
DIMENSION SUB(1001),DIAG(1001),SUP(1001),B(1001)  
IF(N .GT. 1) GO TO 10  
B(1) = B(1)/DIAG(1)  
RETURN  
10 DO 11 K=2,N  
RATIO = -SUB(K)/DIAG(K-1)  
DIAG(K) = DIAG(K) + RATIO*SUP(K-1)  
11 B(K) = B(K) + RATIO*B(K-1)  
B(N) = B(N)/DIAG(N)  
K = N  
DO 12 NP1MK=2,N  
K = K-1  
12 B(K) = (B(K) - SUP(K)*B(K+1))/DIAG(K)  
RETURN  
END
```

```
***  
***
```

```
***  
***  
*** THIS SUBROUTINE CALCULATES THE COEFFICIENT MATRIX [A]3  
*** USED IN THE TRI-DIAGONAL FINITE DIFFERENCE PROCEDURE.  
***
```

```
SUBROUTINE COEFM(BM1,BM2,BM3,FIMK,GMB,GMT,SUBM,DIAM,SUPM)  
IMPLICIT REAL*8(A-H,O-Z)  
COMMON/AREA2/IMAX,IHLOW,IHUP,DY1,DY2,DY3,AMB,AMT,DT  
DIMENSION SUBM(1001),DIAM(1001),SUPM(1001)  
CB = DT/(DY1*DY1)  
CT = DT/(DY3*DY3)  
IMAX1 = IMAX - 1  
SUPM(1) = 0.0  
DIAM(1) = 1.0  
SUBM(1) = 0.0  
SUPM(IMAX) = 0.0  
DIAM(IMAX) = 1.0  
SUBM(IMAX) = 0.0  
DO 1 I=2,IHLOW  
SUBM(I) = -BM1  
SUPM(I) = -BM1  
DIAM(I) = 1. + 2.*BM1  
DO 2 I=IHLOW,IHUP  
SUBM(I) = -BM2  
SUPM(I) = -BM2  
DIAM(I) = 1. + 2.*BM2  
DO 3 I=IHUP,IMAX1  
SUBM(I) = -BM3  
SUPM(I) = -BM3  
DIAM(I) = 1. + 2.*BM3  
SUBM(IHLOW) = -2.*CB*AMB/GMB  
SUPM(IHLOW) = -2.*CB*FIMK/GMB  
DIAM(IHLOW) = 1. + 2.*CB*(AMB+FIMK)/GMB  
SUBM(IHUP) = -2.*CT*FIMK/GMT  
SUPM(IHUP) = -2.*CT*AMT/GMT  
DIAM(IHUP) = 1. + 2.*CT*(AMT+FIMK)/GMT  
RETURN  
END
```

```
***  
***
```

APPENDIX

```
***  
*** THIS SUBROUTINE CALCULATES THE DERIVATIVE OF THETA WITH  
*** RESPECT TO TEMPERATURE.  
***
```

```
SUBROUTINE THETAP(TS,XS,DERIV)  
IMPLICIT REAL*8(A-H,O-Z)  
XOLD = XS  
TCOLD= TS  
CALL CALHTH(TSOLD,XOLD,THOLD)  
TSNEW= 1.0001*TS  
DELTs= TSNEW - TSOLD  
CALL CALX(TSOLD,TSNEW,XOLD,XNEW)  
CALL CALHTH(TSNEW,XNEW,THNEW)  
DERIV = (THNEW - THOLD)/DELTs  
RETURN  
END
```

```
***  
***
```

```
***  
*** THIS SUBROUTINE CALCULATES THE INTEGRAL OF A FUNCTION USING  
*** SIMSON'S RULE  
***
```

```
SUBROUTINE SIMRUL(N,G,DX,SIMS)  
IMPLICIT REAL*8(A-H,O-Z)  
DIMENSION G(1001)  
NK = N-1  
NN = N-2  
G1 = G(1) + G(N)  
G2 = 0.0  
DO 10 K=2,NK,2  
10 G2 = G2+ G(K)  
G3 = 0.0  
IF(NN .EQ. 1) GO TO 15  
DO 11 K=3,NN,2  
11 G3 = G3 + G(K)  
15 SIMS = DX*(G1+4.0*G2+2.0*G3)/3.0  
RETURN  
END  
END OF FILE
```

**END**

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